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(57) 【要約】

【課題】 外装部材とこの中に収納された素電池との間の空隙量を著しく低減することが可能なポリマー電解質二次電池の製造方法を提供する。

【解決手段】 ポリマー電解質素電池を熱融着性樹脂面を持つ外装フィルムで収納した構造のポリマー電解質二次電池を製造する方法において、第1長尺フィルムの熱融着性樹脂面上に複数の前記素電池を前記フィルムの長さ方向に所望の間隔をあけて設置し、第2長尺フィルムの熱融着性樹脂面を複数の前記素電池上面を覆うように重ね、前記第2長尺フィルム上に厚さが前記素電池と同等もしくは僅かに厚いガイド板を少なくとも前記素電池の前記フィルムの長さ方向に沿う側壁に近接するように配置し、前記2枚の長尺フィルムを加熱された一対の弾性ロールの間に通過させて前記各素電池周辺の2枚の長尺フィルムを加熱加圧して熱シールする工程とを具備したことを特徴とする。

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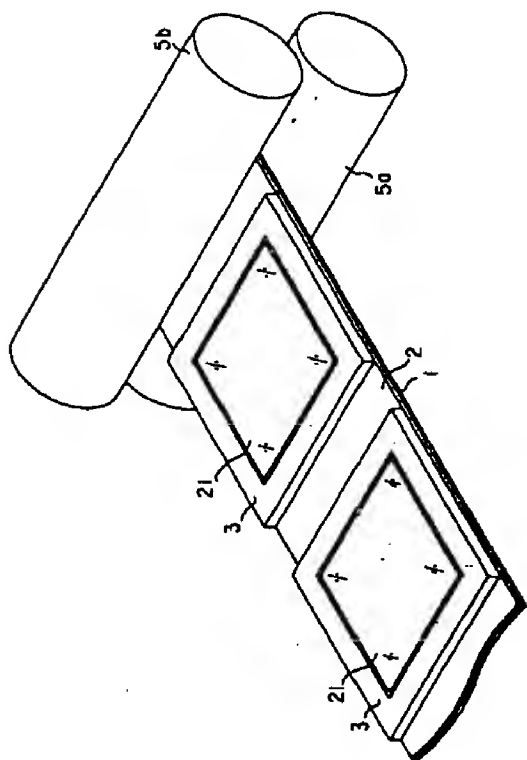
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(57) [Abstract]

[Problem] Manufacturing method of polymer electrolyte secondary battery whose it is possible to decrease void amount with the externally mounted member and unit battery which among these is stored up considerably is offered.

[Means of Solution] Polymer electrolyte unit battery in method which produces polymer electrolyte secondary battery of structure which is stored up with outdoor film which has hot melt adhesion resin surface regarding, Opening desired interval to longitudinal direction of aforementioned film, it installs aforementioned unit battery of plural on hot melt adhesion resin surface of the 1st lengthwise film, In order hot melt adhesion resin surface of 2nd lengthwise film to cover aforementioned unit battery upper surface of the plural, to pile up, In order guide plate where thickness is thick equally to the aforementioned unit battery or barely on aforementioned 2nd lengthwise film proximity to do in side wall which at least parallels to longitudinal direction of the aforementioned film of aforementioned unit battery, it arranges, Is heated passing aforementioned 2 lengthwise film between elastic roll of the pair which heating and pressurizing doing 2 lengthwise film of aforementioned each unit battery periphery, it designates that

step which hot seal is done is possessed as feature.



【特許請求の範囲】

【請求項1】 集電体に活物質および非水電解液を保持するポリマーを含む正極層を積層した正極と、集電体にリチウムイオンを吸蔵放出する炭素質材料を含む負極層を積層した負極と、前記正極の正極層および前記負極の負極層の間に介在された非水電解液を保持するポリマーを含む固体ポリマー電解質層とを備えたポリマー電解質素電池を外装部材で収納した構造のポリマー電解質二次電池を製造する方法において、

第1長尺フィルムの熱融着性樹脂面上に複数の前記素電池を前記フィルムの長さ方向に所望の間隔をあけて設置する工程と、第2長尺フィルムの熱融着性樹脂面を複数の前記素電池上面を覆うように重ねる工程と、前記第2長尺フィルム上に厚さが前記素電池と同等もしくは僅かに厚いガイド板を少なくとも前記各素電池の前記フィルムの長さ方向に沿う側壁に近接するようにそれぞれ配置し、前記ガイド板の底面で前記2枚の長尺フィルムを互いに重ねる工程と、前記複数の素電池を間に挟んだ2枚の長尺フィルムを加熱された一対の耐熱

[Claim(s)]

[Claim 1] Laminates positive electrode layer which includes polymer which keeps active substance and the nonaqueous electrolyte solution in current collector positive electrode which Regarding to method which produces polymer electrolyte secondary battery of structure which stores up polymer electrolyte unit battery which has with negative electrode which laminates negative electrode layer which includes carbonaceous material which lithium ion intercalation and release is done and the solid polymer electrolyte layer which includes polymer which keeps positive electrode layer of the aforementioned positive electrode and nonaqueous electrolyte solution which lies between the negative electrode layer of aforementioned negative electrode with externally mounted member in current collector,

Step which opening desired interval to longitudinal direction of aforementioned film, installs aforementioned unit battery of plural on hot melt adhesion resin surface of the 1st lengthwise film. step which in order to cover aforementioned unit battery upper surface of the plural, repeats hot melt adhesion resin surface of 2nd lengthwise film. In order guide plate where thickness is thick equally to the aforementioned unit battery or barely on aforementioned 2nd lengthwise film proximity to do in side wall which at least parallels to longitudinal direction of

性の弾性ロールの間に通過させて前記各素電池周辺の前記 2 枚の長尺フィルムを加熱加圧してそれらの熱融着樹脂面を熱シールする工程とを具備したことを特徴とするポリマー電解質二次電池の製造方法。

【請求項 2】 前記正極および負極に用いられる集電体のいずれ一方もしくは両者は、前記非水電解液が流通可能な構造を有することを特徴とする請求項 1 記載のポリマー電解質二次電池の製造方法。

【請求項 3】 集電体に活物質および非水電解液を保持するポリマーを含む正極層を積層した正極と、集電体にリチウムイオンを吸蔵放出する炭素質材料を含む負極層を積層した負極と、前記正極の正極層および前記負極の負極層の間に介在された非水電解液を保持するポリマーを含む固体ポリマー電解質層とを備えたポリマー電解質素電池を外装部材で収納した構造のポリマー電解質二次電池を製造する方法において、

第 1 長尺フィルムの熱融着性樹脂面上に複数の前記素電池を前記フィルムの長さ方向に所望の間隔をあけて設置する工程と、前記長尺フィルム上に厚さが前記素電池と同等もしくは僅かに厚い高分子樹脂からなるスペーサを少なくとも前記各素電池の前記フィルムの長さ方向に沿う側壁に接触するようにそれぞれ設置する工程と、第 2 長尺フィルムの熱融着性樹脂面を複数の前記素電池および前記スペーサの上面を覆うように重ねる工程と、前記複数の素電池およびスペーサを間に挟んだ 2 枚の長尺フィルムを加熱された一対の耐熱性の弾性ロールの間に通過させて前記各素電池周辺の前記 2 枚の長尺フィルムを少なくとも前記スペーサを挟んで加熱加圧して熱シールする工程とを具備したことを特徴とするポリマー電解質二次電池の製造方法。

theaforementioned film of aforementioned each unit battery, step which it arranges respectively, repeats aforementioned 2 lengthwise film mutually with bottom surface of aforementioned guide plate. Is heated passing 2 lengthwise film which put between unit battery of theaforementioned plural between between elastic roll of heat resistance of the pair which heating and pressurizing doing aforementioned 2 lengthwise film of theaforementioned each unit battery periphery, manufacturing method of polymer electrolyte secondary battery which designates that step which those hot melt adhesion resin surface hot seal is done is possessed as feature.

[Claim 2] Anyway one side of current collector which is used : or aforementioned positive electrode and negative electrode or as for both, aforementioned nonaqueous electrolyte solution manufacturing method of the polymer electrolyte secondary battery which is stated in Claim 1 which designates that it possesses the structure which is circulation possible as feature.

[Claim 3] Laminates positive electrode layer which includes polymer which keeps active substance and the nonaqueous electrolyte solution in current collector positive electrode which Regarding to method which produces polymer electrolyte secondary battery of structure which stores up polymer electrolyte unit battery which has with negative electrode which laminates negative electrode layer which includes carbonaceous material which lithium ion intercalation and release is done and the solid polymer electrolyte layer which includes polymer which keeps positive electrode layer of theaforementioned positive electrode and nonaqueous electrolyte solution which lies between between the negative electrode layer of aforementioned negative electrode with externally mounted member in current collector,

Step which opening desired interval to longitudinal direction of aforementioned film, installs aforementioned unit battery of plural on hot melt adhesion resin surface of the 1st lengthwise film. step which in order to contact side wall which at least parallel to longitudinal direction of aforementioned film of aforementioned each unit battery, installs spacer which consists of polymer resin where thickness is thick equally to aforementioned unit battery or barely on theaforementioned lengthwise film respectively. step which in order to cover upper surface of aforementioned unit battery and aforementioned spacer of plural, repeats hot melt adhesion resin surface of the 2nd lengthwise film. Is heated passing unit battery of aforementioned plural and 2 lengthwise film which put between spacer between between elastic roll of heat resistance of the pair which manufacturing method of polymer electrolyte secondary battery which designates that it possesses step which putting between aforementioned spacer at least, heating and pressurizing doing, hot seal does aforementioned 2 lengthwise film of theaforementioned each unit battery periphery as feature.

【請求項4】 前記正極および負極に用いられる集電体のいずれ一方もしくは両者は、前記非水電解液が流通可能な構造を有することを特徴とする請求項3記載のポリマー電解質二次電池の製造方法。

【請求項5】 前記スペーサは、熱融着性樹脂からなることを特徴とする請求項3記載のポリマー電解質二次電池の製造方法。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】 本発明は、固体ポリマー電解質層を備えるポリマー電解質二次電池に関するものである。

【0002】

【従来の技術】 近年、電子機器の発達にともない、小型で軽量、かつエネルギー密度が高く、更に繰り返し充放電が可能な二次電池の開発が要望されている。このような二次電池としては、リチウムまたはリチウム合金を活性物質とする負極と、モリブデン、バナジウム、チタンあるいはニオブなどの酸化物、硫化物もしくはセレン化合物を活性物質とする正極とを具備したリチウム二次電池が知られている。しかしながら、リチウムまたはリチウム合金を活性物質とする負極を備えた二次電池は、充放電サイクルを繰り返すと負極にリチウムのデンドライトが発生するため、充放電サイクル寿命が短いという問題点がある。

【0003】 このようなことから、負極に、例えばコークス、黒鉛、炭素繊維、樹脂焼成体、熱分解気相炭素のようなリチウムイオンを吸蔵放出する炭素質材料を用い、 LiPF_6 のような電解質およびエチレンカーボネート、プロピレンカーボネートのような非水溶媒からなる電解液を用いた非水溶媒二次電池が提案されている。前記非水溶媒二次電池は、デンドライト析出による負極特性の劣化を改善することができるため、電池寿命と安全性を向上することができる。

【0004】 一方、米国特許第5,296,318号明細書には正極、負極および電解質層にポリマーを添加することにより柔軟性が付与されたハイブリッドポリマー電解質を有す

[Claim 4] Anyway one side of current collector which is used : or aforementioned positive electrode and negative electrode or as for both, aforementioned nonaqueous electrolyte solution manufacturing method of the polymer electrolyte secondary battery which is stated in Claim 3 which designates that it possesses the structure which is circulation possible as feature.

[Claim 5] As for aforementioned spacer, manufacturing method of polymer electrolyte secondary battery which is stated in Claim 3 which designates that it consists of hot melt adhesion resin as feature.

[Description of the Invention]

[0001]

[Technological Field of Invention] This invention is something regarding polymer electrolyte secondary battery which has solid polymer electrolyte layer.

[0002]

[Prior Art] Recently, attendant upon advancement of electronic equipment, light weight, at the same time energy density is high with miniature, furthermore development of secondary battery where repetitive charge-discharge is possible is demanded. As this kind of secondary battery, lithium secondary battery which possesses with positive electrode which designates negative electrode and molybdenum, vanadium, titanium or niobium or other oxide, the sulfide or selenide which designate lithium or lithium alloy as active substance as the active substance is known. But, secondary battery which has negative electrode which designates lithium or lithium alloy as the active substance, when charge-discharge cycle is repeated, because dendrite of lithium occurs in negative electrode, is a problem that charge-discharge cycle lifetime is short.

[0003] From this kind of thing, nonaqueous solvent secondary battery which uses electrolyte solution which consists of nonaqueous solvent like electrolyte and ethylene carbonate and propylene carbonate like LiPF_6 making use of carbonaceous material which lithium ion like for example coke, graphite, the carbon fiber, resin pyrolyzate and thermally decomposed carbon vapor intercalation and release is done, is proposed to the negative electrode. Because deterioration of negative electrode characteristic with dendrite deposition can be improved, the battery lifetime and safety it can improve aforementioned nonaqueous solvent secondary battery.

[0004] Rechargeable lithium intercalation battery which possesses hybrid polymer electrolyte where on one hand, flexibility is granted by adding polymer to positive electrode, negative

る再充電可能なリチウムインターカレーション電池、つまりポリマー電解質二次電池が開示されている。このようなポリマー電解質二次電池は、集電体に活物質、非水電解液およびこの電解液を保持するポリマーを含む正極層を積層した正極と集電体にリチウムイオンを吸蔵放出し得る炭素質材料、非水電解液およびこの電解液を保持するポリマーを含む負極層を積層した負極との間に非水電解液およびこの電解液を保持するポリマーを含む固体ポリマー電解質層が介在された構造の素電池を備え、この素電池を外装部材内に収納した構造を有する。]

【0005】ところで、前記素電池を前記外装部材内に収納するには、従来、例えばポリエチレンのような熱融着性フィルムから一辺が開口された扁平状の未密封袋を作製し、未密封袋内に前記素電池を挿入し、前記開口部を熱シールして前記素電池を密封袋（外装部材）に収納することが行われている。しかしながら、このような方法で製造されたポリマー電解質二次電池は前記未密封袋内への前記素電池の挿入、開口部の熱シールにおいて十分な脱気となされないために袋状の外装部材と素電池の間に高容量の空隙を生じ、前記素電池からの非水電解液の流出による電池性能を低下を招く問題があった。

【0006】すなわち、ポリマー電解質二次電池は充放電時に前記素電池を構成する正極層、負極層および固体ポリマー電解質層が膨脹・収縮を繰り返すため、それらの中に保持された非水電解液が前記素電池から前記外装部材内にしみ出し易くなる。特に、後述する非水電解液の素電池への供給のために前記素電池を構成する正極および負極の集電体の少なくとも一方がパンチドメタルのような非水電解液が流通し得る構造を有すると、前記充放電時に前記素電池内の非水電解液が前記パンチドメタルからなる集電体を通して前記外装部材内にしみ出し易くなる。従来のポリマー電解質二次電池は前記外装部材と前記素電池の間に高容量の空隙が存在し、前記二次電池の充放電時における前記素電池を構成する正極層、負極層および固体ポリマー電解質層が膨脹を抑制する作用が劣るため、前記素電池からの非水電解液のしみ出しが生じる。また、しみ出した非水電解液は前記空隙に溜まる、つまり素電池内の非水電解液量が低下する。その結果、充放電の繰り返しにより電池容量が急激に低下する問題があった。

electrode and electrolyte layer in the U. S. Patent No. 5,296, 318 specification, in other words polymer electrolyte secondary battery is disclosed. As for this kind of polymer electrolyte secondary battery, In current collector active substance, intercalation and release it can do lithium ion in positive electrode and current collector which laminate positive electrode layer which includes polymer which keeps nonaqueous electrolyte solution and this electrolyte solution carbonaceous material, It has unit battery of structure where solid polymer electrolyte layer which includes polymer which keeps nonaqueous electrolyte solution and this electrolyte solution with negative electrode which laminates the negative electrode layer which includes polymer which keeps nonaqueous electrolyte solution and this electrolyte solution lies between, it possesses structure which stores up this unit battery inside externally mounted member.

[0005] By way, aforementioned unit battery is stored up inside the aforementioned externally mounted member, not yet sealed bag of flat where until recently, one edge is opened from hot melt adhesion film like for example polyethylene is produced, aforementioned unit battery is inserted into not yet sealed bag, the aforementioned opening part hot seal is done and storing up the aforementioned unit battery in sealed bag (externally mounted member) is done. But, as for polymer electrolyte secondary battery which is produced with this kind of method because you cannot do sufficient outgassing in hot seal of insertion and the opening part of aforementioned unit battery to inside aforementioned not yet sealed bag to cause gap of high capacity in externally mounted member of bag and between unit battery, battery performance due to outflow of nonaqueous electrolyte solution from the aforementioned unit battery there was a problem which causes decrease.

[0006] As for namely, polymer electrolyte secondary battery because positive electrode layer, negative electrode layer and solid polymer electrolyte layer which form the aforementioned unit battery at time of charge-discharge repeat expansion *contraction, nonaqueous electrolyte solution which is kept among those from the aforementioned unit battery becomes exuding easy inside aforementioned externally mounted member. Especially, when it possesses structure to which nonaqueous electrolyte solution at least one of current collector of positive electrode and negative electrode which forms aforementioned unit battery for supplying to unit battery of nonaqueous electrolyte solution which it mentions later like the punched metal can circulate, it becomes exuding easy inside the aforementioned externally mounted member through current collector where nonaqueous electrolyte solution inside the aforementioned unit battery consists of aforementioned punched metal at time of aforementioned charge-discharge. As for conventional polymer electrolyte secondary battery gap of high capacity exists between the aforementioned externally

mounted member and aforementioned unit battery, because action where positive electrode layer, negative electrode layer and solid polymer electrolyte layer which form aforementioned unit battery at time of charge-discharge of aforementioned secondary battery control the expansion is inferior, exuding of nonaqueous electrolyte solution from aforementioned unit battery occurs. In addition, exuding is nonaqueous electrolyte solution accumulates in aforementioned gap, in other words amount of nonaqueous electrolyte solution inside unit battery decreases. As a result, there was a problem where battery capacity decreases suddenly with the repetition of charge-discharge.

[0007]

【発明が解決しようとする課題】本発明は、外装部材とこの中に収納された素電池との間の空隙量を著しく低減することが可能なポリマー電解質二次電池の製造方法を提供しようとするものである。

【0008】本発明は、少なくとも平行する2つの側面にスペーサを有する外装部材とこの中に収納された素電池との間の空隙量を著しく低減することが可能なポリマー電解質二次電池の製造方法を提供しようとするものである。

[0009]

【課題を解決するための手段】本発明に係るポリマー電解質二次電池は、集電体に活物質および非水電解液を保持するポリマーを含む正極層を積層した正極と、集電体にリチウムイオンを吸蔵放出する炭素質材料を含む負極層を積層した負極と、前記正極の正極層および前記負極の負極層の間に介在された非水電解液を保持するポリマーを含む固体ポリマー電解質層とを備えたポリマー電解質素電池を外装部材で収納した構造のポリマー電解質二次電池を製造する方法において、第1長尺フィルムの熱融着性樹脂面上に複数の前記素電池を前記フィルムの長さ方向に所望の間隔をあけて設置する工程と、第2長尺フィルムの熱融着性樹脂面を複数の前記素電池上面を覆うように重ねる工程と、前記第2長尺フィルム上に厚さが前記素電池と同等もしくは僅かに厚いガイド板を少なくとも前記各素電池の前記フィルムの長さ方向に沿う側壁に近接するようにそれぞれ配置し、前記ガイド板の底面で前記2枚の長尺フィルムを互いに重ねる工程と、前記複数の素電池を前記ガイド板により間に挟んだ2枚の長尺フィルムを加熱された一対の耐熱性の弾性ロールの間に通過させて前記各素電池周辺の前記2枚の長尺フィルムを加熱加圧してそれらの熱融着樹脂面を熱シールする工程とを具備したことを特徴とするものである。

[0007]

[Problems to be Solved by the Invention] This invention is something which it tries to offer manufacturing method of polymer electrolyte secondary battery whose it is possible to decrease void amount with externally mounted member and the unit battery which among these is stored up considerably.

[0008] This invention is something which it tries to offer manufacturing method of polymer electrolyte secondary battery whose it is possible to decrease void amount with externally mounted member which possesses spacer in 2 side face which is parallel at least and the unit battery which among these is stored up considerably.

[0009]

[Means to Solve the Problems] Relates to this invention as for polymer electrolyte secondary battery which, Laminates positive electrode layer which includes polymer which keeps active substance and the nonaqueous electrolyte solution in current collector positive electrode which, In current collector laminates negative electrode layer which includes carbonaceous material which the lithium ion intercalation and release is done negative electrode which, Regarding to method which produces polymer electrolyte secondary battery of structure which stores up polymer electrolyte unit battery which has with solid polymer electrolyte layer which includes polymer which keeps positive electrode layer of aforementioned positive electrode and nonaqueous electrolyte solution which lies between between negative electrode layer of aforementioned negative electrode with the externally mounted member, step which opening desired interval to longitudinal direction of the aforementioned film, installs aforementioned unit battery of plural on hot melt adhesion resin surface of 1st lengthwise film. step which in order to cover aforementioned unit battery upper surface of the plural, repeats hot melt adhesion resin surface of 2nd lengthwise film. In order guide plate where thickness is thick equally to the aforementioned unit battery or barely on aforementioned 2nd lengthwise film proximity to do in side wall

【0010】本発明に係わる別のポリマー電解質二次電池は、集電体に活物質および非水電解液を保持するポリマーを含む正極層を積層した正極と、集電体にリチウムイオンを吸蔵放出する炭素質材料を含む負極層を積層した負極と、前記正極の正極層および前記負極の負極層の間に介在された非水電解液を保持するポリマーを含む固体ポリマー電解質層とを備えたポリマー電解質素電池を外装部材で収納した構造のポリマー電解質二次電池を製造する方法において、第1長尺フィルムの熱融着性樹脂面上に複数の前記素電池を前記フィルムの長さ方向に所望の間隔をあけて設置する工程と、前記長尺フィルム上に厚さが前記素電池と同等もしくは僅かに厚い高分子樹脂からなるスペーサを少なくとも前記各素電池の前記フィルムの長さ方向に沿う側壁に接触するようにそれぞれ設置する工程と、第2長尺フィルムの熱融着性樹脂面を複数の前記素電池および前記スペーサの上面を覆うように重ねる工程と、前記複数の素電池およびスペーサを間に挟んだ2枚の長尺フィルムを加熱された一対の耐熱性の弾性ロールの間に通過させて前記各素電池周辺の前記2枚の長尺フィルムを少なくとも前記スペーサを挟んで加熱加圧して熱シールする工程とを具備したことを特徴とするものである。

【0011】

【発明の実施の形態】以下、本発明に係るポリマー電解質二次電池の製造方法を図1～図4を参照して詳細に説明する。まず、図1に示すように第1長尺フィルム1の熱融着性樹脂面上に複数の例えば矩形状のポリマー電解質素電池21を前

which at least parallels to longitudinal direction of theaforementioned film of aforementioned each unit battery, step whichit arranges respectively, repeats aforementioned 2 lengthwise film mutuallywith bottom surface of aforementioned guide plate. unit battery of aforementioned plural is heated passing 2 lengthwise filmwhich put between between with aforementioned guide plate between theelastic roll of heat resistance of pair which heating and pressurizing doing theaforementioned 2 lengthwise film of aforementioned each unit battery periphery, it is somethingwhich designates that step which those hot melt adhesion resin surface hot seal is done ispossessed as feature.

[0010] Relates to this invention as for another polymer electrolyte secondary battery which, Laminates positive electrode layer which includes polymer which keeps active substance andthe nonaqueous electrolyte solution in current collector positive electrode which, In current collector laminates negative electrode layer which includes carbonaceous material which thelithium ion intercalation and release is done negative electrode which, Regarding to method which produces polymer electrolyte secondary battery of structure whichstores up polymer electrolyte unit battery which has with solid polymer electrolyte layer which includes polymerwhich keeps positive electrode layer of aforementioned positive electrode and nonaqueous electrolyte solution whichlies between between negative electrode layer of aforementioned negative electrode with theexternally mounted member, step which opening desired interval to longitudinal direction of theaforementioned film, installs aforementioned unit battery of pluralon hot melt adhesion resin surface of 1st lengthwise film. step which in order to contact side wall which at least parallelsto longitudinal direction of aforementioned film of aforementioned eachunit battery, installs spacer which consists of polymer resin where thicknessis thick equally to aforementioned unit battery or barely on theaforementioned lengthwise film respectively, step which in order to cover upper surface of aforementionedunit battery and aforementioned spacer of plural, repeats hot melt adhesion resin surface ofthe 2nd lengthwise film. Is heated passing unit battery of aforementioned plural and 2 lengthwise filmwhich put between spacer between between elastic roll of heat resistance ofthe pair which it is something which designate that it possesses thestep which putting between aforementioned spacer at least, theheating and pressurizing doing, hot seal does aforementioned 2 lengthwise film of theaforementioned each unit battery periphery as feature.

[0011]

[Embodiment of Invention] Below, referring to Figure 1 to Figure 4, you explain manufacturing method of polymer electrolyte secondary batterywhich relates to this invention in detail. First as shown in Figure 1, opening desired interval to longitudinal

記フィルム 1 の長さ方向に所望の間隔をあけて設置する。前記各素電池 21 を前記第 1 長尺フィルム 1 に設置するにあたっては、接着剤を用いて前記長尺フィルム 1 に仮固定することが好ましい。前記素電池 21 は、図 2 に示すように正極 22 と負極 23 との間に固体ポリマー電解質層 24 が介装された構造を有する。前記正極 22 は、正極集電体 25 と、この集電体 25 に担持された正極層 26 から構成されている。前記負極 23 は、負極集電体 27 と、この集電体 27 に担持された負極層 28 とから構成されている。

【0012】次いで、同図 1 に示すように第 2 長尺フィルム 2 の熱融着性樹脂面を複数の前記素電池 21 上面を覆うように重ねた後、前記第 2 長尺フィルム 2 上に厚さが前記素電池 21 と同等もしくは僅かに厚い枠状のガイド板 3 を前記各素電池 21 の周囲側壁に近接するようにそれぞれ配置し、前記ガイド板 3 の底面で前記 2 枚の長尺フィルム 1、2 を互いに重ねる。つづいて、前記複数の素電池 21 が前記ガイド板 3 により間に挟まれた 2 枚の長尺フィルム 1、2 を軸 4 a、4 b を有する耐熱性の弾性ロール 5 a、5 b の間に通過させる。前記ゴムロール 5 a、5 b は、長さが前記長尺フィルム 1、2 の幅よりも十分に長く、かつ所望の加熱源により例えば前記熱融着性樹脂の軟化点以上に加熱されている。図 3 に示すように前記 2 枚の長尺フィルム 1、2 を加熱された前記弾性ロール 5 a、5 b の間に通過させ、前記素電池 21 および前記ガイド板 3 が前記弾性ロール 5 a、5 b の間に移動すると、前記弾性ロール 5 a、5 b が前記素電池 21 および前記ガイド板 3 を包み込むように変形し、前記ガイド板 3 の底面で互いに重ねられた前記 2 枚の長尺フィルム 1、2 において下面側の長尺フィルム 1 部分は前記下部側の弾性ロール 5 a からの熱を受け、上面側の長尺フィルム 2 部分は前記上部側の弾性ロール 5 b から前記枠状のガイド板 3 を通して熱を受けて、それらの熱融着性樹脂面同士が熱シールされる。その結果、前記弾性ロール 5 a、5 b 間を通過させた 2 枚の長尺フィルム 1、2 から前記ガイド板 3 を外し、前記 2 枚の長尺フィルム 1、2 を前記ガイド板 3 周縁が位置された箇所に沿って切断することにより図 4 に示すように素電池 21 とこの素電池 21 を収納し、その周囲側壁付近に位置した枠状の熱シール部 6 を有する熱融着性樹脂面を持つ 2 枚のフィルム 7 a、7 b により形成された外装部材 8 とから構成されたポリマー電解質二次電池 9 が製造される。

direction of theaforementioned film 1, it installs polymer electrolyte unit battery 21 of for example rectangle of plural on hot melt adhesion resin surface of 1st lengthwise film 1. When aforementioned each unit battery 21 is installed in aforementioned 1st lengthwise film 1, to do it is desirable temporary affixion to do in aforementioned lengthwise film 1 making use of adhesive and. Aforementioned unit battery 21, as shown in Figure 2, has structure where the solid polymer electrolyte layer 24 is introduced with positive electrode 22 and negative electrode 23. Aforementioned positive electrode 22 is formed from positive electrode layer 26 which is borne in the positive electrode collector 25 and this current collector 25. Aforementioned negative electrode 23 is formed from negative electrode layer 28 which is borne in the negative electrode collector 27 and this current collector 27.

[0012] Next, way it shows in same Figure 1, in order hot melt adhesion resin surface of 2nd lengthwise film 2 to cover aforementioned unit battery 21 upper surface of plural, after repeating, in order the guide plate 3 of frame where thickness is thick equally to theaforementioned unit battery 21 or barely on aforementioned 2nd lengthwise film 2 proximity to do in periphery side wall of aforementioned each unit battery 21, it arranges respectively, repeats aforementioned 2 lengthwise film 1, 2 mutually with bottom surface of aforementioned guide plate 3. Continuing, unit battery 21 of aforementioned plural it passes 2 lengthwise film 1, 2 which was put between between by aforementioned guide plate 3 between the elastic roll 5a, 5b of heat resistance which possesses axial 4a, 4b. Aforementioned rubber roll 5a, 5b length is long in fully in comparison with width of aforementioned lengthwise film 1, 2, is heated to softening point or higher of the for example aforementioned hot melt adhesion resin at same time by desired heat source. As shown in Figure 3, is heated passing aforementioned 2 lengthwise film 1, 2 between aforementioned elastic roll 5a, 5b which, Aforementioned unit battery 21 and aforementioned guide plate 3 move between theaforementioned elastic roll 5a, 5b when, In order for aforementioned elastic roll 5a, 5b to wrap aforementioned unit battery 21 and aforementioned guide plate 3, it becomes deformed, lengthwise film 1 portion of under side receives heat from elastic roll 5a of theaforementioned bottom side in aforementioned 2 lengthwise film 1, 2 which is repeated mutually with bottom surface of aforementioned guide plate 3, as for lengthwise film two portions of top side receiving heat through guide plate 3 of aforementioned frame from elastic roll 5b of aforementioned upper side, those hot melt adhesion resin surface are done the hot seal. As a result, From 2 lengthwise film 1, 2 which passes between aforementioned elastic roll 5a, 5b theaforementioned guide plate 3 to remove, As shown in Figure 4 by cutting off aforementioned 2 lengthwise film 1, 2 alongside site where aforementioned guide plate 3 peripheral edge is located, the unit battery 21 and this unit battery 21 are stored up, polymer electrolyte secondary

【0013】次に、素電池21を構成する固体ポリマー電解質層24、正極集電体25、正極層26、負極集電体27および負極層28と、長尺フィルム1、2、ガイド板3および弾性ロール5a、5bについて説明する。

【0014】1) 固体ポリマー電解質層24

このポリマー電解質層24は非水電解液及びこの電解液を保持するポリマーを含む。

【0015】前記非水電解液は、非水溶媒に電解質を溶解することにより調製される。前記非水溶媒としては、エチレンカーボネート(EC)、プロピレンカーボネート(PC)、ブチレンカーボネート(BC)、ジメチルカーボネート(DMC)、ジエチルカーボネート(DEC)、エチルメチルカーボネート(EMC)、γ-ブチロラクトン(γ-BL)、スルホラン、アセトニトリル、1,2-ジメトキシエタン、1,3-ジメトキシプロパン、ジメチルエーテル、テトラヒドロフラン(THF)、2-メチルテトラヒドロフラン等を挙げることができる。前記非水溶媒は、単独で使用しても、2種以上混合して使用しても良い。

【0016】前記電解質としては、例えば、過塩素酸リチウム(LiClO_4)、六フッ化リン酸リチウム(LiPF_6)、ホウ四フッ化リチウム(LiBF_4)、六フッ化砒素リチウム(LiAsF_6)、トリフルオロメタンスルホン酸リチウム(LiCF_3SO_3)、ビストリフルオロメチルスルホニルイミドリチウム $[\text{LiN}(\text{CF}_3\text{SO}_3)_2]$ 等のリチウム塩を挙げることができる。

【0017】前記電解質の前記非水溶媒に対する溶解量は、 0.2 mol/l ～ 2 mol/l とすることが望ましい。前記非水電解液を保持するポリマーとしては、例えば、ポリエチレンオキサライド誘導体、ポリプロピレンオキサライド誘導体、前記誘導体を含むポリマー、ビニリデンフロライド(VdF)とヘキサフルオロプロピレン(HFP)との共重合体等を用いることができる。前記固体電解質層において、このようなポリマーは、分子間が架橋された形態で存在していても良い。また、前記共重合体において、VdFは共重合体の骨格部で機械的強度の向上に寄与し、HFPは前記共重合体に非晶質の状態に取り込まれ、非水電解液の保持とリチウムイオンの透過部として機能する。前記HFPの共重合割合は、前記共重合体の合成方法にも依存するが、通常、最大で20重量%前後である。

battery 9 which is formed from the externally mounted member 8 which was formed it is to be possesses hot seal section 6 of frame by 2 film 7a and 7b which have hot melt adhesion resin surface which in position of periphery side wall vicinity is produced.

[0013] Next, you explain concerning solid polymer electrolyte layer 24, positive electrode collector 25, positive electrode layer 26, the negative electrode collector 27 and negative electrode layer 28 and lengthwise film 1, 2, guide plate 3 and elastic roll 5a, 5b which form the unit battery 21.

[0014] 1) solid polymer electrolyte layer 24

This polymer electrolyte layer 24 includes polymer which keeps a nonaqueous electrolyte solution and this electrolyte solution.

[0015] Aforementioned nonaqueous electrolyte solution is manufactured by melting electrolyte in the nonaqueous solvent. As aforementioned nonaqueous solvent, ethylene carbonate (EC), propylene carbonate (PC), butylene carbonate (BC), the dimethyl carbonate (DMC), diethyl carbonate (DEC), ethyl methyl carbonate (EMC), γ-butyrolactone (γ-BL), sulfolane, acetonitrile, the 1,2-dimethoxyethane, 1,3-dimethoxy propane, dimethyl ether, tetrahydrofuran (THF) and 2-methyl tetrahydrofuran etc can be listed. Using and 2 kinds or more mixing, it is good using aforementioned nonaqueous solvent, with alone.

[0016] As aforementioned electrolyte, for example lithium perchlorate (LiClO_4), lithium hexafluorophosphate (LiPF_6), lithium tetrafluoroborate (LiBF_4), the lithium hexafluoroarsenate (LiAsF_6), lithium trifluoromethane sulfonate (LiCF_3SO_3) and lithium bis-(trifluoromethyl sulfonyl) imide $[\text{LiN}(\text{CF}_3\text{SO}_3)_2]$ or other lithium salt can be listed.

[0017] As for dissolved amount for aforementioned nonaqueous solvent of aforementioned electrolyte, it is desirable to make 0.2 mol/l to 2 mol/l . polymer, vinylidene fluoride (VdF) and copolymer etc of hexafluoropropylene (HFP) which include the for example polyethylene oxide derivative, polypropylene oxide derivative and aforementioned derivative as polymer which keeps the aforementioned nonaqueous electrolyte solution, can be used. In aforementioned solid electrolyte layer as for this kind of polymer, intermolecular is good existing with shape which crosslinking is done. In addition, VdF contributes to improvement of mechanical strength with skeleton of copolymer in aforementioned copolymer, HFP is taken in by aforementioned copolymer with state of amorphous, functions as permeable part of retention and lithium ion of nonaqueous electrolyte solution. copolymerization ratio of aforementioned

【0018】前記固体電解質層24は、例えば、以下に説明する方法により作製することができる。

(1) 前記非水電解液を保持するポリマーの溶液を調製し、前記溶液に例えばDBP（ジブチルフタレート）などの可塑剤を添加し、これを成膜、乾燥した後、これを非水電解液中に浸漬し、前記ポリマーに前記電解液を保持させると共に前記可塑剤と前記電解液を置換することによって前記電解液を含浸させることによりポリマー電解質層を作製する。

【0019】(2) 前記非水電解液を保持するポリマーの溶液を調製し、前記溶液に例えばDBP（ジブチルフタレート）などの可塑剤を添加し、これを成膜、乾燥した後、前記可塑剤をエタノール等の溶剤で抽出させる等によって除去し、これに非水電解液を含浸させることによりポリマー電解質層を作製する。

【0020】(3) 前記非水電解液を保持するポリマーの溶液を調製し、これを成膜、乾燥した後、非水電解液を含浸させることによってポリマー電解質層を作製する。前記(1)及び(2)の方法において、可塑剤は、前記固体電解質層の強度等の機械的特性の改善や電解液含浸量を向上させて充放電特性を改善する目的で添加される。前記可塑剤を添加した後、成膜し、前記可塑剤と非水電解液が置換されるようにポリマー電解質層に非水電解液を含浸させることによって、非水電解液を前記ポリマーのみならず前記可塑剤が占めていた空間にも含浸させることができるため、電解液含浸量を増大させることができる。

【0021】なお、前記(1)～(3)の製造方法において、電解液の含浸（可塑剤添加の場合は可塑剤の除去も含む）は、電解液未含浸の素電池を組み立てた後、或いは図4に示す外装部材8に素電池21を収納した後でもよい。

【0022】2) 正極集電体25

この正極集電体25は、アルミニウムからなるパンチドメタ

HFP depends on also synthetic method of theaforementioned copolymer, but usually, with maximum it is approximately a 20 weight %.

[0018] It can produce aforementioned solid electrolyte layer 24, with method which is explained below for example.

(1) As solution of polymer which keeps aforementioned nonaqueous electrolyte solution is manufactured, for example DBP (dibutyl phthalate) or other plasticizer is added to aforementioned solution, the film formation, after drying this, this is soaked in nonaqueous electrolyte solution, theaforementioned electrolyte solution is kept in aforementioned polymer, polymer electrolyte layer is produced by impregnating aforementioned electrolyte solution with theaforementioned plasticizer and substituting aforementioned electrolyte solution.

[0019] (2) It manufactures solution of polymer which keeps aforementioned nonaqueous electrolyte solution, adds for example DBP (dibutyl phthalate) or other plasticizer to aforementioned solution, film formation, after drying this, aforementioned plasticizer it removes with ethanol or other solvent it extracts with such as, it produces polymer electrolyte layer by impregnating nonaqueous electrolyte solution in this.

[0020] (3) Solution of polymer which keeps aforementioned nonaqueous electrolyte solution is manufactured, polymer electrolyte layer is produced film formation, after drying this, by impregnating nonaqueous electrolyte solution. Regarding to method of aforementioned (1) and (2), plasticizer, improvement and electrolyte solution impregnation amount of strength or other mechanical property of aforementioned solid electrolyte layer improving, is added with object which improve charge-discharge characteristic. After adding aforementioned plasticizer, film formation it does, in order for the aforementioned plasticizer and nonaqueous electrolyte solution to be substituted, because the nonaqueous electrolyte solution it can impregnate even in space which aforementioned polymer furthermore aforementioned plasticizer has occupied by impregnating nonaqueous electrolyte solution in polymer electrolyte layer, electrolyte solution impregnation amount can be increased.

[0021] Furthermore, impregnation (In case of plasticizer addition also removal of plasticizer includes.) of electrolyte solution after assembling the unit battery of electrolyte solution unimpregnated, or after storing up unit battery 21 in externally mounted member 8 which is shown in Figure 4 even is good in manufacturing method of aforementioned (1) to (3).

[0022] 2) positive electrode collector 25

As for this positive electrode collector 25, nonaqueous electrolyte

ルのような非水電解液が流通可能な構造のものを用いることができる。なお、非水電解液が流通可能な構造の正極集電体としては、パンチドメタルの他にアルミニウム製メッシュ、アルミニウム製エキスパンドメタル等を用いることができる。また、前記正極集電体は非水電解液が流通可能な構造のもの他に、アルミニウム箔を用いることができる。

【0023】3) 正極層26

前記正極層26は、活物質、導電性材料、非水電解液及びこの電解液を保持するポリマーを含む。

【0024】前記活物質としては、種々の酸化物（例えば LiMn_2O_4 などのリチウムマンガ複合酸化物、二酸化マンガ、例えば LiNiO_2 などのリチウム含有ニッケル酸化物、例えば LiCoO_2 などのリチウム含有コバルト酸化物、リチウム含有ニッケルコバルト酸化物、リチウムを含む非晶質五酸化バナジウムなど）や、カルコゲン化合物（例えば、二硫化チタン、二硫化モリブテンなど）等を挙げることができる。中でも、リチウムマンガ複合酸化物、リチウム含有コバルト酸化物、リチウム含有ニッケル酸化物を用いるのが好ましい。

【0025】前記導電性材料としては、例えば、人造黒鉛、カーボンブラック（例えばアセチレンブラックなど）、ニッケル粉末等を挙げることができる。前記非水電解液及び前記ポリマーは、前述した固体ポリマー電解質層で説明したものと同様なものが用いられる。

【0026】前記正極22は、例えば以下に説明する方法によって作製することができる。

(1) 前記非水電解液を保持するポリマーの溶液を調製し、前記溶液に例えばDBP（ジブチルフタレート）などの可塑剤、前記活物質及び前記導電材料を添加した後、これらを混合し、成膜することにより正極層を作製した後、前記正極層と前記集電体とを例えば熱圧着等によって接合する。これを非水電解液中に浸漬することによって前記ポリマーに前記電解液を保持させると共に前記正極層中の可塑剤と前記電解液を置換することによって前記正極層に電解液を含浸させるか、または前記正極層中の前記可塑剤をエタノール等の溶剤で抽出する等によって除去した後、前記正極層に非水電解液を含浸させることにより正極を作製する。

te solution like punched metal which consists of the aluminum can use those of structure which is circulation possible. Furthermore, aluminum mesh and aluminum expanded metal etc can be used for other than punched metal nonaqueous electrolyte solution as positive electrode collector of structure which is circulation possible. In addition, aforementioned positive electrode collector nonaqueous electrolyte solution can use aluminum foil for other than those of structure which is circulation possible.

[0023] 3) positive electrode layer 26

Aforementioned positive electrode layer 26 includes polymer which keeps active substance, the electrically conductive material, nonaqueous electrolyte solution and this electrolyte solution.

[0024] As aforementioned active substance, various oxide (includes for example LiMn_2O_4 or other lithium manganese composite oxide, manganese dioxide, for example LiNiO_2 or other lithium containing nickel oxide, for example LiCoO_2 or other lithium containing cobalt oxide, lithium containing nickel cobalt oxide and the lithium such as amorphous vanadium pentoxide which) and, chalcogen compound (Such as for example titanium disulfide and molybdenum disulfide) etc can be listed. It is desirable even among them to use lithium manganese composite oxide, lithium containing cobalt oxide and the lithium containing nickel oxide.

[0025] As aforementioned electrically conductive material, for example artificial graphite and carbon black (Such as for example acetylene black), nickel powder etc can be listed. As for aforementioned nonaqueous electrolyte solution and aforementioned polymer, it can use those which are similar to those which are explained with the solid polymer electrolyte layer which is mentioned earlier.

[0026] It can produce aforementioned positive electrode 22, with method which is explained below for example.

(1) It manufactures solution of polymer which keeps aforementioned nonaqueous electrolyte solution, for example DBP (dibutyl phthalate) or other plasticizer and aforementioned active substance and after adding the aforementioned electrically conductive material, it mixes these to aforementioned solution, after producing positive electrode layer by film formation doing, aforementioned positive electrode layer and it glues with aforementioned current collector for example thermobonding etc with. As aforementioned electrolyte solution is kept in aforementioned polymer, by soaking this in nonaqueous electrolyte solution electrolyte solution is impregnated in the aforementioned positive electrode layer with plasticizer in aforementioned positive electrode layer and substituting

【0027】(2) 前記非水電解液を保持するポリマーの溶液を調製し、前記溶液に例えばDBP（ジブチルフタレート）などの可塑剤、前記活物質及び前記導電材料を添加した後、これらを混合し、正極用塗料を調製する。前記正極用塗料を前記集電体に塗工した後、乾燥させる。これを非水電解液中に浸漬することによって前記ポリマーに前記電解液を保持させると共に前記正極層中の可塑剤と前記電解液を置換することによって前記正極層に電解液を含浸させるか、または前記正極層中の前記可塑剤をエタノール等の溶剤で抽出する等によって除去した後、前記正極層に非水電解液を含浸させることにより正極を作製する。

【0028】(3) 前記非水電解液を保持するポリマーの溶液を調製し、前記溶液に前記活物質及び前記導電材料を添加した後、これらを混合し、成膜することにより正極層を作製した後、前記正極層と前記集電体とを例えば熱圧着等によって接着し、非水電解液を含浸させることによって正極を作製する。

【0029】(4) 前記非水電解液を保持するポリマーの溶液を調製し、前記溶液に前記活物質及び前記導電材料を添加した後、これらを混合し、正極用塗料を調製する。前記正極用塗料を前記集電体に塗工した後、乾燥させ、非水電解液を含浸させることによって正極を作製する。

【0030】前記(1)及び(2)の方法において、可塑剤は前記固体電解質層の強度等の機械的特性の改善や電解液含浸量を向上させて充放電特性を改善する目的で添加される。

aforementioned electrolyte solution, Or aforementioned plasticizer in aforementioned positive electrode layer positive electrode is produced with ethanol or other solvent after removing it extracts with such as, by impregnating nonaqueous electrolyte solution in aforementioned positive electrode layer.

[0027] (2) Solution of polymer which keeps aforementioned nonaqueous electrolyte solution is manufactured, for example DBP (dibutyl phthalate) or other plasticizer and aforementioned electrically conductive material, these are mixed to aforementioned solution, the paint for positive electrode is manufactured. After painting paint for aforementioned positive electrode in the aforementioned current collector, it dries. As aforementioned electrolyte solution is kept in aforementioned polymer, by soaking this in nonaqueous electrolyte solution electrolyte solution is impregnated in the aforementioned positive electrode layer with plasticizer in aforementioned positive electrode layer and substituting aforementioned electrolyte solution, Or aforementioned plasticizer in aforementioned positive electrode layer positive electrode is produced with ethanol or other solvent after removing it extracts with such as, by impregnating nonaqueous electrolyte solution in aforementioned positive electrode layer.

[0028] (3) It manufactures solution of polymer which keeps aforementioned nonaqueous electrolyte solution, aforementioned active substance and after adding aforementioned electrically conductive material, it mixes these to aforementioned solution, after producing the positive electrode layer by film formation doing, aforementioned positive electrode layer and it glues with the aforementioned current collector for example thermobonding etc with it produces positive electrode by impregnating nonaqueous electrolyte solution.

[0029] (4) Solution of polymer which keeps aforementioned nonaqueous electrolyte solution is manufactured, aforementioned active substance and after adding the aforementioned electrically conductive material, these are mixed to aforementioned solution, the paint for positive electrode is manufactured. After painting paint for aforementioned positive electrode in the aforementioned current collector, drying, it produces positive electrode by impregnating the nonaqueous electrolyte solution.

[0030] Regarding to method of aforementioned (1) and (2), plasticizer improvement and electrolyte solution impregnation amount of strength or other mechanical property of aforementioned solid electrolyte layer improving, is added with objective which improves charge-discharge characteristic.

【0031】なお、前記(1)～(4)の方法において、電解液の含浸(可塑剤添加の場合は可塑剤の除去も含む)は、電解液未含浸の素電池を組み立てた後、或いは図4に示す外装部材8に素電池21を収納した後でもよい。

【0032】4) 負極集電体27

この負極集電体27は、銅からなるパンチドメタルのような非水電解液が流通可能な構造のものを用いることができる。なお、非水電解液が流通可能な構造の正極集電体としては、パンチドメタルの他に銅製メッシュ、銅製エキスパンドメタル等を用いることができる。また、前記負極集電体は非水電解液が流通可能な構造のもの他に銅箔を用いることができる。

【0033】5) 負極層28

この負極層28は、リチウムイオンを吸蔵放出する炭素質材料と、非水電解液と、この電解液を保持するポリマーを含有する。

【0034】前記リチウムイオンを吸蔵放出する炭素質材料としては、例えば、有機高分子化合物(例えば、フェノール樹脂、ポリアクリロニトリル、セルロース等)を焼成することにより得られるもの、コークスや、ピッチを焼成することにより得られるもの、人造グラファイト、天然グラファイト等に代表される炭素質材料を挙げることができる。中でも、アルゴンガス、窒素ガス等の不活性ガス雰囲気中において、500℃～3000℃の温度で、常圧または減圧下にて前記有機高分子化合物を焼成して得られる炭素質材料を用いるのが好ましい。

【0035】前記非水電解液及び前記ポリマーは、前述した固体ポリマー電解質層で説明したものと同等なものが用いられる。なお、前記負極層28は人造グラファイト、天然グラファイト、カーボンブラック、アセチレンブラック、ケッチェンブラック、ニッケル粉末、ポリフェニレン誘導体等の導電性材料、オレフィン系ポリマーや炭素繊維等のフィラーを含むことを許容する。

【0036】前記負極23は、例えば以下に説明する方法によって作製することができる。

(1) 前記非水電解液を保持するポリマーの溶液を調製し、

[0031] Furthermore, regarding to method of aforesaid (1) to (4), the impregnation (In case of plasticizer addition also removal of plasticizer includes.) of electrolyte solution after assembling unit battery of the electrolyte solution unimpregnated, or after storing up unit battery 21 in externally mounted member 8 which is shown in the Figure 4 even is good.

[0032] 4) negative electrode collector 27

As for this negative electrode collector 27, nonaqueous electrolyte solution like punched metal which consists of the copper can use those of structure which is circulation possible. Furthermore, copper mesh and copper expanded metal etc can be used for other than punched metal nonaqueous electrolyte solution as positive electrode collector of structure which is circulation possible. In addition, aforesaid negative electrode collector nonaqueous electrolyte solution can use copper foil for other than those of structure which is circulation possible.

[0033] 5) negative electrode layer 28

This negative electrode layer 28 contains polymer which keeps carbonaceous material and nonaqueous electrolyte solution and this electrolyte solution which lithium ion intercalation and release are done.

[0034] Are acquired by calcining for example organic polymer compound (Such as for example phenolic resin, polyacrylonitrile and cellulose) intercalation and release is done the aforesaid lithium ion as carbonaceous material which, those which. Those which are acquired by calcining coke and pitch. carbonaceous material which is represented in artificial graphite and natural graphite etc can be listed. With temperature of 500 °C to 3000 °C, calcining aforesaid organic polymer compound under the ambient pressure or vacuum in in argon gas and nitrogen gas or other inert gas atmosphere, it is desirable even among them to use carbonaceous material which is acquired.

[0035] As for aforesaid nonaqueous electrolyte solution and aforesaid polymer, it can use those which are similar to those which are explained with the solid polymer electrolyte layer which is mentioned earlier. Furthermore, aforesaid negative electrode layer 28 allows fact that the artificial graphite, natural graphite, carbon black, acetylene black, Ketjen Black, nickel powder, the polyphenylene derivative or other electrically conductive material, olefin polymer and carbon fiber or other filler are included.

[0036] It can produce aforesaid negative electrode 23, with method which is explained below for example.

(1) It manufactures solution of polymer which keeps aforesaid

前記溶液に例えばDBP（ジブチルフタレート）などの可塑剤、前記活物質を添加した後、これらを混合し、成膜することにより負極層を作製した後、前記負極層と前記集電体とを例えば熱圧着等によって接着する。これを非水電解液中に浸漬することによって前記ポリマーに前記電解液を保持させると共に前記負極層中の可塑剤と前記電解液を置換することによって前記負極層に電解液を含浸させるか、または前記負極層中の前記可塑剤をエタノール等の溶剤で抽出する等によって除去した後、非水電解液を含浸させることにより負極を作製する。

【0037】（2）前記非水電解液を保持するポリマーの溶液を調製し、前記溶液に例えばDBP（ジブチルフタレート）などの可塑剤、前記活物質を添加した後、これらを混合し、負極用塗料を調製する。前記負極用塗料を前記集電体に塗工した後、乾燥させる。これを非水電解液中に浸漬することによって前記ポリマーに前記電解液を保持させると共に前記負極層中の可塑剤と前記電解液を置換することによって前記負極層に電解液を含浸させるか、または前記負極層中の前記可塑剤をエタノール等の溶剤で抽出する等によって除去した後、非水電解液を含浸させることにより負極を作製する。

【0038】（3）前記非水電解液を保持するポリマーの溶液を調製し、前記溶液に前記活物質を添加した後、これらを混合し、成膜することにより負極層を作製した後、前記負極層と前記集電体とを例えば熱圧着等によって接着する。これに非水電解液を含浸させることにより負極を作製する。

【0039】（4）前記非水電解液を保持するポリマーの溶液を調製し、前記溶液に前記活物質を添加した後、これらを混合し、負極用塗料を調製する。前記負極用塗料を前記集電体に塗工した後、乾燥させ、非水電解液を含浸させることにより負極を作製する。

ioned nonaqueous electrolyte solution, after adding for example DBP (dibutyl phthalate) or other plasticizer and aforementioned active substance in the aforementioned solution, it mixes these, after producing negative electrode layer by the film formation doing, aforementioned negative electrode layer and it glues with the aforementioned current collector for example thermobonding etc with. As aforementioned electrolyte solution is kept in aforementioned polymer, bysoaking this in nonaqueous electrolyte solution electrolyte solution is impregnated in the aforementioned negative electrode layer with plasticizer in aforementioned negative electrode layer and substituting aforementioned electrolyte solution, Or aforementioned plasticizer in aforementioned negative electrode layer negative electrode is produced with ethanol or other solvent after removing it extracts with such as, by impregnating nonaqueous electrolyte solution.

[0037] (2) Solution of polymer which keeps aforementioned nonaqueous electrolyte solution is manufactured, after adding for example DBP (dibutyl phthalate) or other plasticizer and aforementioned active substance in the aforementioned solution, these are mixed, paint for negative electrode is manufactured. After painting paint for aforementioned negative electrode in the aforementioned current collector, it dries. As aforementioned electrolyte solution is kept in aforementioned polymer, bysoaking this in nonaqueous electrolyte solution electrolyte solution is impregnated in the aforementioned negative electrode layer with plasticizer in aforementioned negative electrode layer and substituting aforementioned electrolyte solution, Or aforementioned plasticizer in aforementioned negative electrode layer negative electrode is produced with ethanol or other solvent after removing it extracts with such as, by impregnating nonaqueous electrolyte solution.

[0038] (3) It manufactures solution of polymer which keeps aforementioned nonaqueous electrolyte solution, after adding aforementioned active substance to aforementioned solution, it mixes these, after producing negative electrode layer by film formation doing, the aforementioned negative electrode layer and it glues with aforementioned current collector for example thermobonding etc with. negative electrode is produced by impregnating nonaqueous electrolyte solution in this.

[0039] (4) Solution of polymer which keeps aforementioned nonaqueous electrolyte solution is manufactured, after adding aforementioned active substance to the aforementioned solution, these are mixed, paint for negative electrode is manufactured. After painting paint for aforementioned negative electrode in the aforementioned current collector, drying, it produces negative electrode by impregnating the nonaqueous electrolyte solution.

【0040】前記(1)及び(2)の方法において、可塑剤は、前記固体電解質層の強度等の機械的特性の改善や電解液含浸量を向上させて充放電特性を改善する目的で添加される。

【0041】なお、前記(1)～(4)の方法において、電解液の含浸(可塑剤添加の場合は可塑剤の除去も含む)は、電解液未含浸の素電池を組み立てた後、或いは図4に示す外装部材8に素電池21を収納した後でもよい。

【0042】また、電解液未含浸の素電池を組み立てた後、或いは図4に示す外装部材8に素電池21を収納した後に非水電解液を含浸する場合には、前記正極集電体25および前記負極集電体27のいずれか一方もしくは両者がパンチドメタルのような非水電解液が流通可能な構造のものを用いることが好ましい。

【0043】6) 長尺フィルム1、2

この長尺フィルム1、2は、少なくとも対向する面がポリエチレンのような熱融着性樹脂からなる。前記長尺フィルム1、2は、具体的には熱融着性樹脂フィルム単体；熱融着性樹脂フィルムにポリエチレンテレフタレート、ナイロンのような樹脂フィルムまたはAl箔、銅箔のような金属箔をラミネートしたもの；を用いることができる。このようなラミネートフィルムを長尺フィルムとして用いる場合には、前記素電池側に前記熱融着性樹脂フィルムが位置するように配置する。

【0044】7) ガイド板3

このガイド板3は、熱融着性樹脂に対して非熱シール性の材料から形成すればよく、特に熱伝導性が良好な銅やアルミニウムのような金属から形成されることが好ましい。

【0045】ガイド板は、前述した図1に示す枠状のものに限らず、図5に示すように長尺フィルム2を複数の素電池21上に重ねた後、この長尺フィルム2上に2つの細長状のガイド板3a、3bを前記各素電池21の前記フィルム2の長さ方向に沿う側壁に近接するように配置してもよい。

【0046】8) 弾性ロール5a、5b

これらの弾性ロール5a、5bは、前記長尺フィルム1、2

[0040] Regarding to method of aforementioned (1) and (2), plasticizer, improvement and electrolyte solution impregnation amount of strength or other mechanical property of aforementioned solid electrolyte layer improving, is added with objective which improves charge-discharge characteristic.

[0041] Furthermore, regarding to method of aforementioned (1) to (4), the impregnation (In case of plasticizer addition also removal of plasticizer includes.) of electrolyte solution after assembling unit battery of the electrolyte solution unimpregnated, or after storing up unit battery 21 in externally mounted member 8 which is shown in the Figure 4 even is good.

[0042] In addition, after assembling unit battery of electrolyte solution unimpregnated, when or after storing up unit battery 21 in externally mounted member 8 which is shown in Figure 4 then a nonaqueous electrolyte solution is impregnated, nonaqueous electrolyte solution any one or both of the aforementioned positive electrode collector 25 and aforementioned negative electrode collector 27 like punched metal using those of structure which is circulation possible is desirable.

[0043] 6) lengthwise film 1, 2

This lengthwise film 1, 2 consists of hot melt adhesion resin surface which opposes at least like polyethylene. Concretely hot melt adhesion resin film unit; those which laminate metal foil like resin film or the Al foil and copper foil like polyethylene terephthalate and nylon in hot melt adhesion resin film; you can use aforementioned lengthwise film 1, 2. When this kind of laminate film it uses, as lengthwise film in order for the aforementioned hot melt adhesion resin film to be located on aforementioned unit battery side, it arranges.

[0044] 7) guide plate 3

This guide plate 3 vis-a-vis hot melt adhesion resin if from non hot seal characteristic material it should have formed, it is desirable to be formed from the metal like copper and aluminum where especially thermal conductivity is satisfactory.

[0045] As shown in Figure 5 not just those of frame which is shown in the Figure 1 which is mentioned earlier, after repeating lengthwise film 2 on the unit battery 21 of plural, in order on this lengthwise film 2 it is long and narrow guide plate 3a, 3b, condition proximity to do in side wall which parallels to longitudinal direction of aforementioned film 2 of the aforementioned each unit battery 21, it is possible to arrange guide plate.

[0046] 8) elastic roll 5a, 5b

As for these elastic roll 5a, 5b, from fact that it is heated in order

を熱融着するために加熱されることから、前記フィルムの軟化点温度に耐えられるものであるが必要で、例えばシリコーンゴム、フッ素ゴム等を用いることができる。

【0047】なお、前記弾性ロール5a、5b間を通して前記第1、第2の長尺フィルムを互いに熱融着した後、電池形状を安定化させるために熱融着した前記第1、第2の長尺フィルムを加熱されていない別の弾性ロール間を通して冷却することを許容する。

【0048】以上説明した本発明に係るポリマー電解質二次電池の製造方法は、例えば図1に示すように第1長尺フィルム1の熱融着性樹脂面上に複数の素電池21を前記フィルム1の長さ方向に所望の間隔をあけて設置する工程と、第2長尺フィルム2の熱融着性樹脂面を複数の前記素電池21上面を覆うように重ねる工程と、前記第2長尺フィルム2上に厚さが前記素電池21と同等もしくは僅かに厚い枠状のガイド板3を前記各素電池21の周囲側壁に近接するようにそれぞれ配置し、前記ガイド板3の底面で前記2枚の長尺フィルム1、2を互いに重ねる工程と、前記複数の素電池21を前記ガイド板3により間に挟んだ2枚の長尺フィルム1、2を加熱された一対の耐熱性の弾性ゴムロール5a、5bの間を通して前記各素電池21周辺の前記2枚の長尺フィルム1、2を加熱加圧してそれらの熱融着樹脂面を互いに熱シールする工程とを具備する。

【0049】このような方法によれば、図4に示すように素電池21はその周囲に熱シール部6を有する2枚のフィルム7a、7bからなる外装部材8で覆われ、前記素電池21の正極、負極側の面に前記フィルム7a、7bを密着しているため、前記素電池21と前記外装部材8間に殆ど空隙がない状態で前記素電池21を収納できる。その結果、前記素電池21の充放電時に前記素電池21を構成する正極層26、負極層28および固体ポリマー電解質層24が膨脹・収縮を繰り返しても、前記素電池21の正極、負極側の面に密着した前記外装部材8の2枚のフィルム7a、7bにより抑えることができるため、各構成部材の膨脹・収縮によりそれらの中の非水電解液が滲み出するのを抑制できる。特に、前記素電池の正極および負極のいずれか一方もしくは両者にパンチドメタルのような非水電解液が流通可能な構造の集電体を用いた場合、前記素電池21の各構成部材の膨脹・収縮によりそれらの中の非水電解液がより滲み出し易くなるが、前記外装部材8の2枚のフィルム7a、7bにより前記滲み出しを効

r hot melt adhesion to do aforementioned lengthwise film 1, 2, it is something which withstands the softening point of aforementioned film, but being necessary, you can use the for example silicone rubber and fluororubber etc.

[0047] Furthermore, aforementioned 1st, second lengthwise film mutually hot melt adhesion after doing, battery shape in order to be stabilized aforementioned 1st which hot melt adhesion is done, passing between another elastic roll which through second lengthwise film is not heated through between aforementioned elastic roll 5a, 5b, it allows fact that it cools.

[0048] Above as for manufacturing method of polymer electrolyte secondary battery which relates to this invention which is explained, as shown in for example Figure 1, step which opening desired interval to longitudinal direction of aforementioned film 1, installs unit battery 21 of the plural on hot melt adhesion resin surface of 1st lengthwise film 1. step which in order to cover aforementioned unit battery 21 upper surface of the plural, repeats hot melt adhesion resin surface of 2nd lengthwise film 2. In order guide plate 3 of frame where thickness is thick equally to the aforementioned unit battery 21 or barely on aforementioned 2nd lengthwise film 2 the proximity to do in periphery side wall of aforementioned each unit battery 21, step which it arranges respectively, repeats aforementioned 2 lengthwise film 1, 2 mutually with bottom surface of aforementioned guide plate 3. unit battery 21 of aforementioned plural is heated passing 2 lengthwise film 1, 2 which put between between with aforementioned guide plate 3 between the elastic rubber roll 5a, 5b of heat resistance of pair which heating and pressurizing doing the aforementioned 2 lengthwise film 1, 2 of aforementioned each unit battery 21 periphery, those hot melt adhesion resin surface mutually it possesses with step which hot seal is done.

[0049] According to this kind of method, as shown in Figure 4, as for the unit battery 21 it is covered with externally mounted member 8 which consists of 2 film 7a and the 7b which possess hot seal section 6 in periphery because the positive electrode of aforementioned unit battery 21, aforementioned film 7a, it has stuck 7b on aspect of negative electrode side, between aforementioned unit battery 21 and aforementioned externally mounted member 8 almost it can store up the aforementioned unit battery 21 with state which does not have gap. As a result, nonaqueous electrolyte solution among those oozing puts out positive electrode layer 26, negative electrode layer 28 and the solid polymer electrolyte layer 24 which form aforementioned unit battery 21 at time of charge-discharge of the aforementioned unit battery 21 expansion * contraction over again, because it is impossible, to hold down positive electrode of aforementioned unit battery 21, the 2 film 7a of aforementioned externally mounted member 8 which it sticks

果的に抑制できる。また、前記素電池 21 を各構成部材の膨脹・収縮によりそれらの中の非水電解液が滲み出そうとしても、前記素電池 21 と前記外装部材 8 間に殆ど空隙がないため、滲み出し量を低減できる。したがって、充放電の繰返しによる素電池 21 内の非水電解液量の低下を抑制できるため、長期間亘って高い容量を有するポリマー電解質二次電池を得ることができる。

【0050】また、複数の素電池 21 を前記ガイド板 3 により間に挟んだ 2 枚の長尺フィルム 1、2 を加熱された一対の耐熱性の弾性ロール 5a、5b の間に通過させる際、厚さが前記素電池 21 と同等もしくは僅かに厚い枠状のガイド板 3 を前記各素電池 21 の周囲側壁に近接するように配置することによって、前記素電池 21 に弾性ロール 5a、5b の圧力が加わるのを抑制できる。その結果、前記弾性ロール 5a、5b 間に複数の素電池 21 を前記ガイド板 3 により間に挟んだ 2 枚の長尺フィルム 1、2 を通過させる際、前記素電池 21 に既に非水電解液が含まれていても、前記素電池 21 からの電解液の滲み出しを抑制することができる。

【0051】なお、前述した図 5 に示すように複数の素電池 21 上に第 2 長尺フィルム 2 を重ねた後、この長尺フィルム 2 上に 2 つの細長状のガイド板 3a、3b を前記各素電池 21 の前記フィルム 2 の長さ方向に沿う側壁に近接するように配置した状態で弾性ロール 5a、5b を通過させた場合にも、枠状のガイド板を用いたのと同様な効果を有するポリマー電解質二次電池を得ることができる。ただし、枠状のガイド板を用いた方が長尺フィルムの長さ方向のみならず、その幅方向に沿う前記素電池の側壁、つまり素電池の周囲側壁にシール性が良好な熱シール部を形成できる。したがって、素電池が収納された外装部材内の空隙量を著しく低減できるため、図 5 に示す 2 枚のガイド板 3a、3b を用いる場合より充放電の繰返しによる素電池 21 内の非水電解液量の低下をより効果的に抑制することができる。

to aspect of the negative electrode side, with 7b with expansion * contraction of each constituting component can control. Especially, when nonaqueous electrolyte solution like punched metal in any one or both of the positive electrode and negative electrode of aforementioned unit battery current collector of structure which is circulation possible is used, nonaqueous electrolyte solution among those it becomes the exuding easier depending upon expansion * contraction of each constituting component of the aforementioned unit battery 21. Aforementioned exuding can be controlled in the effective, but 2 film 7a of aforementioned externally mounted member 8, with 7b. In addition, trying, that nonaqueous electrolyte solution among those oozing will put out the aforementioned unit battery 21 with expansion * contraction of each constituting component, because almost there is not a gap between aforementioned unit battery 21 and aforementioned externally mounted member 8, it can decrease exuding quantity. Therefore, because decrease of amount of nonaqueous electrolyte solution inside unit battery 21 due to the repetition of charge-discharge can be controlled, long period extending, it can acquire polymer electrolyte secondary battery which possesses high capacity.

[0050] In addition, Occasion where it passes between elastic roll 5a, 5b of heat resistance of the pair which 2 lengthwise film 1, 2 which put between unit battery 21 of plural between with aforementioned guide plate 3 is heated, in order guide plate 3 to the frame where thickness is thick equally to aforementioned unit battery 21 or barely proximity to do in periphery sidewall of aforementioned each unit battery 21, the fact that pressure of elastic roll 5a, 5b joins to aforementioned unit battery 21 by arranging, can be controlled. As a result, occasion where 2 lengthwise film 1, 2 which put between unit battery 21 of plural between between aforementioned elastic roll 5a, 5b with the aforementioned guide plate 3 is passed, nonaqueous electrolyte solution being already impregnated in the aforementioned unit battery 21, exuding of electrolyte solution from the aforementioned unit battery 21 can be controlled.

[0051]

【0052】次に、本発明に係る別のポリマー電解質二次電池の製造方法を図6～図8を参照して詳細に説明する。まず、図6に示すように第1長尺フィルム1の熱融着性樹脂面に前述した構造の複数の矩形状のポリマー電解質素電池21を前記フィルム1の長さ方向に所望の間隔をあけて設置する。前記各素電池21を前記第1長尺フィルム1に設置するにあたっては、例えば前記各素電池21の裏面に接着剤をポイント的に付着させて前記長尺フィルム1に仮固定するすることが好ましい。つづいて、前記長尺フィルム1上に厚さが前記素電池21と同等もしくは僅かに厚い高分子樹脂からなる枠状のスペーサ10を前記各素電池21の周囲側壁に接触するようにそれぞれ設置する。ひきつづき、第2長尺フィルム1の熱融着性樹脂面を前記素電池21および前記スペーサ10の上面を覆うように重ねた後、前記複数の素電池21およびスペーサ10を間に挟まれた2枚の長尺フィルム1、2を軸4a、4bを有する耐熱性の弾性ロール5a、5bの間に通過させる。前記弾性ロール5a、5bは、長さが前記長尺フィルム1、2の幅よりも十分に長く、かつ所望の加熱源により例えば前記熱融着樹脂の軟化点以上に加熱されている。図7に示すように前記2枚の長尺フィルム1、2を加熱された前記弾性ロール5a、5bの間に通過させ、前記素電池21および前記スペーサ10が前記弾性ロール5a、5bの間に移動すると、前記弾性ロール5a、5bが前記素電池21および前記スペーサ10を包み込むように変形し、前記2枚の長尺フィルム1、2が前記弾性ロール5a、5bからの熱を受け、前記長尺フィルム1、2が前記枠状のスペーサ10の上下面にそれぞれ熱シールされる。この後、前記弾性ロール5a、5b間を通過させた2枚の長尺フィルム1、2を前記スペーサ10の周縁の沿って切断することにより図8に示すように素電池21と、この素電池21を収納し、その周囲側壁に枠状スペーサ10およびこのスペーサ10に熱シールされた熱融着性樹脂面を持つ2枚のフィルム7a、7bとにより形成された外装部材11とから構成されたポリマー電解質二次電池12が製造される。

【0053】前記長尺フィルム1、2は、少なくとも対向する面がポリエチレンのような熱融着性樹脂からなる。前記長尺フィルム1、2は、具体的には熱融着性樹脂フィルム単体：熱融着性樹脂フィルムにポリエチレンテレフタレート、ナイロンのような樹脂フィルムまたはAl箔、銅箔のような金

[0052] Next, referring to Figure 6 to Figure 8, you explain manufacturing method of another polymer electrolyte secondary battery which relates to this invention in detail. First, as shown in Figure 6, opening desired interval to longitudinal direction of the aforementioned film 1, it installs polymer electrolyte unit battery 21 of rectangle of plural of construction which is mentioned earlier on hot melt adhesion resin surface of 1st lengthwise film 1. When aforementioned each unit battery 21 is installed in aforementioned 1st lengthwise film 1, it is desirable in back surface of for example aforementioned each unit battery 21 depositing point, temporary affixion to do adhesive in the aforementioned lengthwise film 1 and to do. Continuing, in order to contact periphery side wall of aforementioned each unit battery 21, it installs spacer 10 of frame which consists of polymer resin where thickness is thick equally to aforementioned unit battery 21 or barely on aforementioned lengthwise film 1 respectively. After in order to cover upper surface of aforementioned unit battery 21 and the aforementioned spacer 10, repeating hot melt adhesion resin surface of continuation and the 2nd lengthwise film 1, unit battery 21 of aforementioned plural and 2 lengthwise film 1, 2 which was put between spacer 10 between are passed between elastic roll 5a, 5b of the heat resistance which possesses axial 4a 4b. Aforementioned elastic roll 5a, 5b length is long in fully in comparison with width of aforementioned lengthwise film 1, 2, is heated to softening point or higher of the for example aforementioned hot melt adhesion make resin at same time by the desired heat source. As shown in Figure 7, is heated passing aforementioned 2 lengthwise film 1, 2 between aforementioned elastic roll 5a, 5b which, When aforementioned unit battery 21 and aforementioned spacer 10 move between aforementioned elastic roll 5a, 5b, in order for aforementioned elastic roll 5a, 5b to wrap aforementioned unit battery 21 and aforementioned spacer 10, it becomes deformed, aforementioned 2 lengthwise film 1, 2 receives heat from the aforementioned elastic roll 5a, 5b, aforementioned lengthwise film 1, 2 hot seal makes respectively top and bottom surfaces of spacer 10 of aforementioned frame. As shown in Figure 8 by margin (edge) of aforementioned spacer 10 paralleling, cutting off 2 lengthwise film 1, 2 which passes after this and between the aforementioned elastic roll 5a, 5b, it stores up unit battery 21 and this unit battery 21, the polymer electrolyte secondary battery 12 which is formed from externally mounted member 11 which was formed in periphery side wall by with 2 film 7a and 7b which have hot melt adhesion resin surface which hot seal is done in frame spacer 10 and this spacer 10 is produced.

[0053] Aforementioned lengthwise film 1, 2 consists of hot melt adhesion resin surface which opposes at least like polyethylene. Concretely hot melt adhesion resin film unit; those which laminate metal foil like resin film or the Al foil and copper foil like polyethylene terephthalate and nylon in hot melt

層箔をラミネートしたもの：を用いることができる。このようなラミネートフィルムを長尺フィルムとして用いる場合には、前記素電池側に前記熱融着性樹脂フィルムが位置するように配置する。

【0054】前記スペーサは、例えばポリエチレンのような熱融着性樹脂またはポリプロピレン、ナイロン等の高分子樹脂等からなる。特に、熱融着性樹脂からなるスペーサは前記弾性ロール5a、5bによる加熱、加圧時に長尺フィルム1、2に対して良好に熱シールすることが可能になる。

【0055】前記スペーサは、前述した図6に示す枠状のものに限らず、図9に示すように長尺フィルム1に複数の素電池21をその長さ方向に所望の間隔をあけて設置した後、2つの細長状のスペーサ10a、10bを前記各素電池21の前記フィルム1の長さ方向に沿う側壁にそれぞれ接触するように配置してもよい。このような細長状のスペーサ10a、10bを前記第1長尺フィルム1に設置するにあたっては、前記スペーサ10a、10bの裏面に接着剤をポイント的に付着させて前記長尺フィルム1に仮固定することが好ましい。

【0056】前記スペーサには、収納される素電池の正負極の集電体を外部に引き出すための一対の端子を取り付けることを許容する。前記弾性ロール5a、5bは、前述したのと同様、前記長尺フィルム1、2を熱融着するために加熱されることから、前記フィルムの軟化点温度に耐えられるものであるが必要で、例えばシリコンゴム、フッ素ゴム等を用いることができる。

【0057】なお、前記弾性ロール5a、5b間を通して前記第1、第2の長尺フィルムを前記スペーサ10に熱融着した後、電池形状を安定化させるために熱融着した前記第1、第2の長尺フィルムを加熱されていない別の弾性ロール間を通して冷却することを許容する。

【0058】以上説明した本発明に係る別のポリマー電解質二次電池の製造方法は、例えば図6に示すように第1長尺フィルム1の熱融着性樹脂面上に複数の素電池21を前記フィルム1の長さ方向に所望の間隔をあけて設置する工程と、前記長尺フィルム1上に厚さが前記素電池21と同等もしくは僅かに厚い高分子樹脂からなる枠状のスペーサを前記各素電池21の周囲側壁に接触するようにそれぞれ設置する工程と、第2長尺フィルム2の熱融着性樹脂面を複数の前記素電池

adhesion resin film; you can use aforementioned lengthwise film 1, 2. When this kind of laminate film it uses, as lengthwise film in order for the aforementioned hot melt adhesion resin film to be located on aforementioned unit battery side, it arranges.

[0054] Aforementioned spacer, consists of hot melt adhesion resin or polypropylene and the nylon or other polymer resin etc like for example polyethylene. Especially, as for spacer which consists of hot melt adhesion resin when heating and pressurization with aforementioned elastic roll 5a, 5b it becomes satisfactorily hot seal possible vis-a-vis lengthwise film 1, 2 to do.

[0055] Aforementioned spacer as shown in Figure 9 not just the use of the frame which is shown in Figure 6 which is mentioned earlier, after opening desired interval to longitudinal direction, installing unit battery 21 of plural in the lengthwise film 1, 2 long and narrow in order to contact side wall which parallels to longitudinal direction of aforementioned film 1 of the aforementioned each unit battery 21 respectively, may arrange spacer 10a, 10b of condition. When this kind of spacer 10a, 10b of condition is installed long and narrow in aforementioned 1st lengthwise film 1, it is desirable in back surface of the aforementioned spacer 10a, 10b depositing point, temporary affixation to do adhesive in aforementioned lengthwise film 1 and to do.

[0056] fact that terminal of pair in order to pull out the current collector of positive/negative electrode of unit battery which is stored up to outside is installed is allowed in aforementioned spacer. As for aforementioned elastic roll 5a, 5b, that you mentioned earlier, similarity, from fact that it is heated in order hot melt adhesion to do the aforementioned lengthwise film 1, 2, it is something which withstands softening point of aforementioned film, but being necessary, you can use the for example silicone rubber and fluororubber etc.

[0057] Furthermore, aforementioned 1st, second lengthwise film hot melt adhesion after doing, battery shape in order to be stabilized aforementioned 1st which hot melt adhesion is done, passing to aforementioned spacer 10 between another elastic roll which through second lengthwise film is not heated through between the aforementioned elastic roll 5a, 5b, it allows fact that it cools.

[0058] Above as for manufacturing method of another polymer electrolyte secondary battery which relates to this invention which is explained, as shown in for example Figure 6, step which opening the desired interval to longitudinal direction of aforementioned film 1, installs unit battery 21 of the plural on hot melt adhesion resin surface of 1st lengthwise film 1. step which in order to contact periphery side wall of aforementioned each unit battery 21, installs spacer of frame

21および前記スペース10の上面を覆うように重ねる工程と、前記複数の素電池21およびスペース10を間に挟んだ2枚の長尺フィルム1、2を加熱された一対の耐熱性の弾性ロール5a、5bの間に通過させて前記各素電池周辺の前記2枚の長尺フィルム1、2を前記枠状のスペース10を挟んで加熱加圧して熱シールする工程を具備する。

which consists of the polymer resin where thickness is thick equally to aforementioned unit battery 21 or barely in 1 on aforementioned lengthwise film respectively. step which in order to cover upper surface of aforementioned unit battery 21 and aforementioned spacer 10 of plural, repeats hot melt adhesion resin surface of the 2nd lengthwise film 2. Is heated passing unit battery 21 of aforementioned plural and 2 lengthwise film 1, 2 which put between spacer 10 between between elastic roll 5a, 5b of heat resistance of the pair which it possesses step which putting between spacer 10 of aforementioned frame, heating and pressurizing doing, hot seal does the aforementioned 2 lengthwise film 1, 2 of aforementioned each unit battery periphery.

【0059】このような方法によれば、図8に示すように素電池21はその周囲側壁に枠状スペース10およびこのスペース10に熱融着性樹脂面が熱シールされた2枚のフィルム7a、7bとにより形成されたに外装部材11で覆われ、前記素電池21の正極、負極側の面に前記フィルム7a、7bが密着されているため、前記素電池21と前記外装部材11間に殆ど空隙がない状態で前記素電池21を収納できる。その結果、前記素電池21の充放電時に前記素電池21を構成する正極層、負極層および固体ポリマー電解質層が膨脹・収縮を繰り返しても、前記素電池21の正極、負極側の面に密着した前記外装部材11の2枚のフィルム7a、7bにより抑えることができるため、各構成部材の膨脹・収縮によりそれらの中の非水電解液が滲み出するのを抑制できる。特に、前記素電池の正極および負極のいずれか一方もしくは両者にパンチドメタルのような非水電解液が流通可能な構造の集電体を用いた場合、前記素電池21の各構成部材の膨脹・収縮によりそれらの中の非水電解液がより滲み出し易くなるが、前記外装部材11の2枚のフィルム7a、7bにより前記滲み出しを効果的に抑制できる。また、前記素電池21を各構成部材の膨脹・収縮によりそれらの中の非水電解液が滲み出そうとしても、前記素電池21と前記外装部材11間に殆ど空隙がないため、滲み出し量を低減できる。したがって、充放電の繰り返しの素電池21内の非水電解液量の低下を抑制できるため、長期間亘って高い容量を有するポリマー電解質二次電池を得ることができる。

[0059] In this kind of method we depend, As shown in Figure 8 unit battery 21 in periphery side wall hot melt adhesion resin surface hot seal was done in frame spacer 10 and this spacer 10: film 7a, It was formed by with 7b with externally mounted member 11 to be covered, because the positive electrode of aforementioned unit battery 21, aforementioned film 7a, the 7b has stuck on aspect of negative electrode side, between aforementioned unit battery 21 and aforementioned externally mounted member 11 almost aforementioned unit battery 21 can be stored up with state which does not have gap. As a result nonaqueous electrolyte solution among those oozing puts out positive electrode layer, negative electrode layer and the solid polymer electrolyte layer which form aforementioned unit battery 21 at time of charge-discharge of the aforementioned unit battery 21 expansion * contraction over again, because it is impossible, to hold down positive electrode of aforementioned unit battery 21, the 2 film 7a of aforementioned externally mounted member 11 which it sticks to aspect of the negative electrode side, with 7b with expansion * contraction of each constituting component you can control. Especially, when nonaqueous electrolyte solution like punched metal in any one or both of the positive electrode and negative electrode of aforementioned unit battery current collector of structure which is circulation possible is used, nonaqueous electrolyte solution among those it becomes the exuding easier depending upon expansion * contraction of each constituting component of the aforementioned unit battery 21 aforementioned exuding can be controlled in the effective, but 2 film 7a of aforementioned externally mounted member 11, with 7b. In addition, trying, that nonaqueous electrolyte solution among those oozing will put out the aforementioned unit battery 21 with expansion * contraction of each constituting component, because almost there is not a gap between aforementioned unit battery 21 and aforementioned externally mounted member 11, it can decrease exuding quantity. Therefore, because decrease of amount of nonaqueous electrolyte solution inside unit battery 21 can be controlled in repetition of charge-discharge, long period extending, it can acquire polymer electrolyte secondary battery which possesses high capacity.

【0060】また、複数の素電池21および前記枠状のスペーサ10を間に挟んだ2枚の長尺フィルム1、2を加熱された一対の耐熱性の弾性ロール5a、5bの間に通過させる際、厚さが前記素電池21と同等もしくは僅かに厚い枠状のスペーサ10を前記各素電池21の周囲側壁に接触して配置されているため、前記素電池21に弾性ロール5a、5bの圧力が加わるのを抑制できる。その結果、前記弾性ロール5a、5b間に複数の素電池21および前記スペーサ10を間に挟んだ2枚の長尺フィルム1、2を通過させる際、前記素電池21に既に非水電解液が含浸されていても、前記素電池21からの電解液の滲み出しを抑制することができる。

【0061】さらに、外装部材11は周囲に枠状のスペーサ10を有するため、外部からの衝撃を前記スペーサで緩和できるため、信頼性の高いポリマー電解質二次電池を得ることができる。

【0062】なお、前述した図9に示すように第1長尺フィルム1に複数の素電池21をその長さ方向に所望の間隔をあけて設置し、2つの細長状のスペーサ10a、10bを前記各素電池21の前記フィルム1の長さ方向に沿う側壁にそれぞれ接触するように設置した後、前記素電池21およびスペーサ10a、10b上に第2長尺フィルム2を重ねた状態で弾性ロール5a、5bを通過させた場合にも、枠状のスペーサを用いたのと同様な効果を有するポリマー電解質二次電池を得ることができる。ただし、枠状のスペーサを用いた方が長尺フィルムの長さ方向のみならず、その幅方向に沿う前記素電池の側壁、つまり素電池の周囲側壁に接触するスペーサを有する外装部材を形成できることから、図9に示す2枚のスペーサ10a、10bを用いる場合より素電池と外装部材の間の空隙を極めて小さくでき、充放電の繰り返しによる素電池21内の非水電解液量の低下をより効果的に抑制することができる。

【0063】

【実施例】以下、本発明の実施例を前述した図面を参照して詳細に説明する。

(実施例1)

[0060] In addition, Occasion where it passes between elastic roll 5a, 5b of heat resistance of the pair which unit battery 21 of plural and 2 lengthwise film 1, 2 which put between the spacer 10 of aforementioned frame between is heated, because spacer 10 of frame where thickness is thick equally to aforementioned unit battery 21 or barely contacting periphery sidewall of aforementioned each unit battery 21, it is arranged, you can control fact that pressure of elastic roll 5a, 5b joins to aforementioned unit battery 21. As a result, occasion where between aforementioned spacer 10 between are passed between the aforementioned elastic roll 5a, 5b, nonaqueous electrolyte solution being already impregnated in the aforementioned unit battery 21, exuding of electrolyte solution from aforementioned unit battery 21 can be controlled.

[0061] Furthermore, externally mounted member 11 in order to possess spacer 10 of frame in the periphery, because impact from outside can be eased with the aforementioned spacer, can acquire polymer electrolyte secondary battery where reliability is high.

[0062] Furthermore, As shown in Figure 9 which you mention earlier, opening desired interval to the longitudinal direction, it installs unit battery 21 of plural in 1st lengthwise film 1, When 2 long and narrow in order to contact side wall which parallels to longitudinal direction of aforementioned film 1 of the aforementioned each unit battery 21 respectively with aforementioned unit battery 21 and state which repeats 2nd lengthwise film 2 on spacer 10a, 10b after, installing the spacer 10a, 10b of condition, elastic roll 5a, 5b is passed even, spacer of the frame was used with can acquire polymer electrolyte secondary battery which almost possesses similar effect. However, Method which uses spacer of frame longitudinal direction of lengthwise film furthermore, When side wall of aforementioned unit battery which parallels to the lateral direction, in other words from fact that externally mounted member which possesses the spacer which contacts periphery side wall of unit battery can be formed, 2 spacer 10a, 10b which is shown in Figure 9 is used compared to gap between the unit battery and externally mounted member quite it can make small it can control from the decrease of amount of nonaqueous electrolyte solution inside unit battery 21 due to repetition of the charge-discharge in effective.

[0063]

[Working Example(s)] Below, referring to drawing which mentions earlier Working Example of the this invention, you explain in detail.

(Working Example 1)

＜正極の作製＞アセトン20gにビニリデンフロライドヘキサフルオロプロピレン (VdF-HFP) の共重合体 (エルファトケム社製商品名: KYNAR2750、共重合比 [VdF:HFP] が85:15) 粉末2.8gを溶解した後、このアセトン溶液にジブチルフタレート (DBP) 4.3gを添加し、活物質として組成式が LiCoO_2 で表されるリチウム含有コバルト酸化物を10.5gと、導電性材料としてのアセチレンブラック1.13gを添加し、混合、分散させて正極用ペーストを調製した。前記正極用ペーストをアルミニウム製パンチドメタル (穴径: 1.5mm、開孔率40%) からなる正極集電体にナイフコータを用いて2.5mAh/cm² となるよう塗布速度1m/minで塗工し、乾燥空気により塗膜を乾燥することによって正極を作製した。

<Production of positive electrode> After melting copolymer (Elf Atochem supplied tradename; KYNAR2750 and copolymerization ratio [VdF:HFP] 85:15) powder 2.8g of vinylidene fluoride - hexafluoropropylene (VdF - HFP) in acetone 20g, it added dibutyl phthalate (DBP) 4.3g to this acetone solution, composition formula being LiCoO_2 as the active substance, it added acetylene black 1.13g, lithium containing cobalt oxide which is displayed as 10.5g and electrically conductive material it mixed, dispersed and manufactured paste for the positive electrode. paste for aforementioned positive electrode in order to become 2.5 mAh/cm² in the positive electrode collector which consists of aluminum punched metal (hole diameter; 1.5 mm and open pore ratio 40 %) making use of knife coater was painted with application rate 1 m/min, positive electrode was produced by drying coating with dry air.

＜負極の作製＞前記正極層に用いられたのと同様なビニリデンフロライドヘキサフルオロプロピレンの共重合体2.0gをアセトン12gに溶解させた後、このアセトン溶液にジブチルフタレート (DBP) 3.12gを添加し、活物質としてメソフェーズピッチ系炭素繊維 (株式会社ペトカ社製) 7.37gを添加し、これらを混合することにより負極用ペーストを調製した。前記負極用ペーストを銅製パンチドメタル (穴径: 1.5mm、開孔率40%) からなる負極集電体に2.5mAh/cm² となるようナイフコータを用いて前述したのと同様な条件で塗工し、乾燥空気により塗膜を乾燥することによって負極を作製した。

<Production of negative electrode> It was used for aforementioned positive electrode layer, that copolymer 2.0g of the similar vinylidene fluoride - hexafluoropropylene after melting, dibutyl phthalate (DBP) 3.12g was added to this acetone solution in acetone 12g, mesophase pitch type carbon fiber (Petoca, Ltd. supplied) 7.37g was added as active substance, paste for the negative electrode was manufactured by mixing these. paste for aforementioned negative electrode way it becomes 2.5 mAh/cm² in the negative electrode collector which consists of copper punched metal (hole diameter; 1.5 mm and open pore ratio 40 %) that you mentioned earlier making use of knife coater was painted with similar condition, negative electrode was produced by drying coating with dry air.

＜固体ポリマー電解質層の作製＞前記正極層に用いられたのと同様なビニリデンフロライドヘキサフルオロプロピレンとの共重合体2.0gをアセトン10gに溶解させた後、このアセトン溶液にジブチルフタレート (DBP) 2.0gを添加し、混合することによって電解質層用ペーストを調製した。このペーストを平滑なガラス板上に乾燥後の膜厚が70μmになるように塗布した後、乾燥し、前記ガラス板から剥離し、固体ポリマー電解質層を作製した。

<Production of solid polymer electrolyte layer> It was used for aforementioned positive electrode layer, that copolymer 2.0g of the similar vinylidene fluoride - hexafluoropropylene after melting, dibutyl phthalate (DBP) 2.0g was added to this acetone solution in acetone 10g, paste for electrolyte layer was manufactured by mixing. After in order on smooth glass sheet for film thickness after drying to become the 70 μm, applying this paste, it dried, peeled off from the aforementioned glass sheet, produced solid polymer electrolyte layer.

＜非水電解液の調製＞エチレンカーボネート (EC) とジメチルカーボネート (DMC) が体積比で1:1の割合で混合された非水溶媒に電解質としての LiPF_6 をその濃度が1mol/lになるように溶解させて非水電解液を調製した。

<Manufacturing nonaqueous electrolyte solution> Ethylene carbonate (EC) and dimethyl carbonate (DMC) being volume ratio, in order for concentration to become 1 mol/l, melting LiPF_6 as electrolyte in nonaqueous solvent which is mixed at ratio of 1:1, it manufactured nonaqueous electrolyte solution.

＜素電池の作製＞得られた正極および負極を2cm×2cmの大きさに切り出し、前記固体ポリマー電解質層を2.25cm×2.25cmの大きさに切り出した。前記正極と前記負極の間に前記ポリマー電解質層を介在させ、これらを130℃に加熱した剛性ロールにて加熱圧着して電解液未含浸の素電池を得た。つづいて、前記電解液未含浸の素電池を前記

<Production of unit battery> Positive electrode and negative electrode which it acquires was cut in size of 2 cm X 2 cm, the aforementioned solid polymer electrolyte layer was cut in size of 2.25 cm X 2.25 cm. Aforementioned polymer electrolyte layer lying between between aforementioned positive electrode and aforementioned negative electrode,

非水電解液中に2時間浸漬して前記素電池を構成する正極層、負極層およびポリマー電解質層中のDBPと前記電解液を置換して前記電解液を含浸することにより図2に示す構造の素電池を作製した。

[0064] 次いで、前述した図1に示すように厚さ50μmのポリエチレン(PE)フィルムと厚さ50μmのポリエチレンテレフタレート(PET)フィルムとをラミネートした第1長尺フィルム1のPEフィルム上に前述した方法で作製した複数の素電池21を前記フィルム1の長さ方向に所望の間隔をあけてそれぞれ設置すると共に前記素電池裏面にポイント的に付けた接着剤により仮固定した。厚さ50μmのPEフィルムと厚さ50μmのPETフィルムとをラミネートした第2長尺フィルム2のPEフィルム面を複数の前記素電池21上面を覆うように重ねた後、前記第2長尺フィルム2上に厚さが前記素電池21より僅かに厚い銅からなる枠状のガイド板3を前記素電池21の周囲側壁に近接するように配置し、前記ガイド板3の底面で前記2枚の長尺フィルム1、2を互いに重ねた。つづいて、前記複数の素電池21が前記ガイド板3により間に挟まれた2枚の長尺フィルム1、2を軸4a、4bを有するシリコンゴムからなる弾性ロール5a、5bの間に通過させた。前記弾性ロール5a、5bは、長さが前記長尺フィルム1、2の幅よりも十分に長く、かつ所望の加熱源により110℃に加熱されている。図3に示すように前記2枚の長尺フィルム1、2を加熱された前記弾性ロール5a、5bの間に通過させ、前記素電池21および前記ガイド板3が前記弾性ロール5a、5bの間に移動させることにより、前記弾性ロール5a、5bが前記素電池21および前記ガイド板3を包み込むように変形し、前記ガイド板3の底面で互いに重ねられた前記2枚の長尺フィルム1、2部分が互いに熱シールされた。ひきつづき、前記弾性ロール5a、5b間を通過させた2枚の長尺フィルム1、2から前記ガイド板3を外し、前記2枚の長尺フィルム1、2を前記ガイド板3周縁が位置された箇所に沿って切断することにより図4に示すように素電池21とこの素電池21を収納し、その周囲側壁付近に位置した枠状の熱シール部6を有する2枚のPE/PETのラミネートフィルム7a、7bにより形成された外装部材8とから構成されたポリマー電解質二次電池9を製造した。

thermobonding doing with stiffness roll which heats these to 130 °C, it acquired unit battery of electrolyte solution unimpregnated. Continuing, 2 hours soaking unit battery of aforementioned electrolyte solution unimpregnated in the aforementioned nonaqueous electrolyte solution, substituting DBP and the aforementioned electrolyte solution in positive electrode layer, negative electrode layer and polymer electrolyte layer which form the aforementioned unit battery, it produced unit battery of structure which it shows in Figure 2 by impregnating aforementioned electrolyte solution.

[0064] Next, as shown in Figure 1 which is mentioned earlier, a opening the desired interval to longitudinal direction of aforementioned film 1, it installs unit battery 21 of plural which is produced with method which is mentioned earlier on PE film of 1st lengthwise film 1 which laminates with polyethylene (PE) film of the thickness 50 μm and polyethylene terephthalate (PET) film of thickness 50 μm respectively temporary affixion it did with adhesive which you attach to aforementioned unit battery back surface point. In order PE film surface of 2nd lengthwise film 2 which laminates with PE film of the thickness 50 μm and PET film of thickness 50 μm to cover aforementioned unit battery 21 upper surface of the plural, after repeating, in order proximity to do guide plate 3 of the frame which consists of copper where thickness is barely thicker than aforementioned unit battery 21 on aforementioned 2nd lengthwise film 2 in periphery side wall of aforementioned unit battery 21, it arranged, repeated aforementioned 2 lengthwise film 1, 2 mutually with bottom surface of aforementioned guide plate 3. Continuing, unit battery 21 of aforementioned plural it passed 2 lengthwise film 1, 2 which was put between between by aforementioned guide plate 3 between the elastic roll 5a, 5b which consists of silicone rubber which possesses axial 4a, 4b. Aforementioned elastic roll 5a, 5b length is long in fully in comparison with width of aforementioned lengthwise film 1, 2, is heated to 110 °C at the same time by desired heat source. As shown in Figure 3, is heated passing aforementioned 2 lengthwise film 1, 2 between aforementioned elastic roll 5a, 5b which, in order for the aforementioned elastic roll 5a, 5b to wrap aforementioned unit battery 21 and the aforementioned guide plate 3 due to fact that aforementioned unit battery 21 and the aforementioned guide plate 3 move between aforementioned elastic roll 5a, 5b, it became deformed, aforementioned 2 lengthwise film 1, 2 portion which is repeated mutually with bottom surface of aforementioned guide plate 3 was done hot seal mutually. Continuation, From 2 lengthwise film 1, 2 which passes between aforementioned elastic roll 5a, 5b the aforementioned guide plate 3 to remove, As shown in Figure 4 by cutting off aforementioned 2 lengthwise film 1, 2 alongside site where aforementioned guide plate 3 peripheral edge is located, the unit battery 21 and this unit battery 21 were stored up, polymer electrolyte secondary battery 9 which is formed from the

externally mounted member 8 which was formed it is to be possesses hot seal section 6 of frame laminate film 7a of 2 PE/PET which, by 7b inposition of periphery side wall vicinity was produced.

【0065】（実施例2）まず、図6に示すように厚さ50 μ mのPEフィルムと厚さ50 μ mのPETフィルムとをラミネートした第1長尺フィルム1のPEフィルム上に実施例1と同様な素電池21を前記フィルム1の長さ方向に所望の間隔をあけてそれぞれ設置すると共に前記素電池表面にポイント的に付けた接着剤により仮固定した。つづいて、前記長尺フィルム1上に厚さが前記素電池21と同等のポリエチレンからなる枠状のスペーサ10を前記素電池21の周囲側壁に接触するようにそれぞれ設置した。厚さ50 μ mのPEフィルムと厚さ50 μ mのPETフィルムとをラミネートした第2長尺フィルム2のPE面を前記素電池21および前記スペーサ10の上面を覆うように重ねた後、前記複数の素電池21およびスペーサ10を間に挟まれた2枚の長尺フィルム1、2を軸4a、4bを有するシリコーゴムからなる弾性ロール5a、5bの間に通過させた。前記弾性ロール5a、5bは、長さが前記長尺フィルム1、2の幅よりも十分に長く、かつ所望の加熱源により110°Cに加熱されている。図7に示すように前記2枚の長尺フィルム1、2を加熱された前記弾性ロール5a、5bの間に通過させ、前記素電池21および前記スペーサ10を前記弾性ロール5a、5bの間に移動させることにより、前記弾性ロール5a、5bが前記素電池21および前記スペーサ103を包み込むように変形し、前記長尺フィルム1、2のPEフィルムが前記枠状のスペーサ10の上下面にそれぞれ熱シールされた。ひきつづき、前記弾性ロール5a、5b間を通過させた2枚の長尺フィルム1、2を前記スペーサ10の周縁の沿って切断することにより図8に示すように素電池21と、この素電池21を収納し、その周囲側壁に枠状スペーサ10およびこのスペーサ10に熱シールされた2枚のPE/PETのラミネートフィルム7a、7bとにより形成された外装部材11とから構成されたポリマー電解質二次電池12を製造した。

【0066】（比較例）内容積が実施例1と同様な素電池に近似し、一辺が開口した厚さ50 μ mのPEフィルムと厚さ50 μ mのPETフィルムとをラミネートした構造の未密封袋を作製し、この未密封袋の開口部から前記素電池を挿入し、前記開口部を熱シールすることにより外装部材である密封袋内に素電池が収納されたポリマー電解質二次電池を製造した。

[0065] (Working Example 2) First, as shown in Figure 6, as opening desired interval to longitudinal direction of theaforementioned film 1, it installs unit battery 21 which is similar to theWorking Example 1 in PE film of thickness 50 m and on PE film of 1st lengthwise film 1 which laminates PET film of thickness 50 m respectively temporary affixion it did withthe adhesive which you attach to aforementioned unit battery back surface point. Continuing, in order to contact periphery side wall of aforementioned unit battery 21,it installed spacer 10 of frame which consists of polyethylene wherethe thickness is equal to aforementioned unit battery 21 on aforementionedlengthwise film 1 respectively. After in order to cover upper surface of aforementioned unit battery 21 and theaforementioned spacer 10, repeating P E face of 2nd lengthwise film 2 which laminateswith PE film of thickness 50 m and PET film of thickness 50 m, unit battery 21 ofthe aforementioned plural and 2 lengthwise film 1, 2 which was put between spacer 10between were passed between elastic roll 5a, 5b which consists of silico -rubber which possesses axial 4a, 4b Aforementioned elastic roll 5a, 5b length is long in fully in comparisonwith width of aforementioned lengthwise film 1, 2, is heated to 110 °C atthe same time by desired heat source . As shown in Figure 7, is heated passing aforementioned 2 lengthwise film 1, 2between aforementioned elastic roll 5a, 5b which, in order for theaforementioned elastic roll 5a, 5b to wrap aforementioned unit battery 21 and theaforementioned spacer 103 with aforementioned unit battery 21 and moving theaforementioned spacer 10 between aforementioned elastic roll 5a, 5b, it became deformed, PE film of aforementioned lengthwise film 1, 2 hot seal made respectively top and bottom surfaces of spacer 10 of aforementioned frame. As shown in Figure 8 by surrounding edge of aforementioned spacer 10paralleling, cutting off 2 lengthwise film 1, 2 which passes during continuingand aforementioned elastic roll 5a, 5b, it stored up unit battery 21 and this unit battery 21,it produced polymer electrolyte secondary battery 12 which is formed from externally mounted member 11 which was formed in periphery side wall laminate film 7a of 2 PE/ PET which hot seal is done, by withthe 7b in frame spacer 10 and this spacer 10.

[0066] (Comparative Example) It closely resembled to unit battery where internal volume is similar to theWorking Example 1, it produced not yet sealed bag of structure which laminates withthe PE film of thickness 50 m which one edge opens and PET film of thethickness 50 m, inserted aforementioned unit battery from opening part of this notyet sealed bag, it produced polymer electrolyte secondary battery where unit

【0067】得られた実施例1、2および比較例の二次電池について、収納された素電池の正極集電体および負極集電体をリードを用いて外部に引き出し、充電電流2mA、4.2V、10時間の定電流定電圧充電を行った後、2.7Vまで2mAの電流で放電する充放電を繰り返し行った。100回の充放電を繰り返した後の初期容量に対する放電容量維持率を測定した。その結果を下記表1に示す。

【0068】

表1	
放電容量維持率 (%)	
実施例1	85
実施例2	70
比較例	17

前記表1から明らかなように本実施例1、2により得られた二次電池は、比較例の二次電池に比べて放電容量維持率が極めて高いことがわかる。これは、実施例1、2の二次電池の外装フィルム、外装部材を構成する2枚のPE/PETのラミネートフィルムが素電池の正極、負極側の面に密着していること、素電池が収納された外装部材内の殆ど空隙が生じていないことに起因する。

【0069】

【発明の効果】以上詳述したように本発明によれば、外装部材とこの中に収納された素電池との間の空隙量を著しく低減して充放電時における前記素電池の膨脹・収縮に起因する非水電解液の滲み出しを抑制し、ひいては長期間亘って高い容量を有するポリマー電解質二次電池の製造方法を提供することができる。

【図面の簡単な説明】

【図1】本発明に係るポリマー電解質二次電池の製造を説明するための斜視図。

battery is stored up inside the sealed bag which is an externally mounted member by hot seal doing aforementioned opening part.

[0067] Concerning secondary battery of Working Example 1, 2 and Comparative Example which it acquires, the positive electrode collector and negative electrode collector of unit battery which is stored up were pulled out to outside making use of lead, after doing constant current constant voltage charging of charging current 2 mA, 4.2V and 10 hours, charge-discharge which discharges with the current of 2 mA repeatedly was done to 2.7V. After repeating charge-discharge of 100 times, discharge capacity maintenance ratio for initial capacity was measured. Result is shown in below-mentioned Table 1.

[0068]

As been clear from aforementioned Table 1, as for secondary battery which is acquired with this working example 1, 2, it understands that discharge capacity maintenance ratio quite is high in comparison with secondary battery of Comparative Example. external mounting film of secondary battery of Working Example 1, 2, laminate film of 2 PE/PET which forms externally mounted member positive electrode of unit battery, has stuck this, to aspect of negative electrode side, it originates in inside externally mounted member where unit battery is stored up almost gap not occurring.

[0069]

[Effects of the Invention] As above detailed, according to this invention, decreasing void amount with the externally mounted member and unit battery which among these is stored up considerably, you control exuding of nonaqueous electrolyte solution which originates in expansion * contraction of aforementioned unit battery at time of charge-discharge, the consequently long period extend and you can offer manufacturing method of polymer electrolyte secondary battery which possesses the high capacity.

[Brief Explanation of the Drawing(s)]

[Figure 1] Oblique view in order to explain production of polymer electrolyte secondary battery which relates to this invention.

【図 2】本発明に用いられる素電池の部分切欠斜視図。

【図 3】図 1 の弾性ロール付近の部分拡大断面図。

【図 4】図 1 に示す方法により製造されたポリマー電解質二次電池の部分切欠斜視図。

【図 5】本発明に係るポリマー電解質二次電池の他の製造形態を説明するための斜視図。

【図 6】本発明に係る別のポリマー電解質二次電池の製造を説明するための斜視図。

【図 7】図 6 の弾性ロール付近の部分拡大断面図。

【図 8】図 6 に示す方法により製造されたポリマー電解質二次電池の部分切欠斜視図。

【図 9】本発明に係る別のポリマー電解質二次電池における他の製造形態を説明するための斜視図。

【符号の説明】

- 1...第 1 長尺フィルム、
- 2...第 2 長尺フィルム、
- 3、3 a、3 b...ガイド板、
- 5 a、5 b...弾性ロール、
- 6...熱シール部、
- 7 a、7 b...熱融着性樹脂面を持つフィルム
- 8、11...外装部材、
- 9、12...ポリマー電解質二次電池、
- 10、10 a、10 b...スペーサ、
- 21...素電池、
- 22...正極、

[Figure 2] Partially cut-out oblique diagram of unit battery which is used for this invention.

[Figure 3] Portion enlarged cross section diagram of elastic roll vicinity of Figure 1.

[Figure 4] Partially cut-out oblique diagram of polymer electrolyte secondary battery which is produced by method which is shown in Figure 1.

[Figure 5] Oblique view in order to explain other production form of polymer electrolyte secondary battery which relates to this invention.

[Figure 6] Oblique view in order to explain production of another polymer electrolyte secondary battery which relates to this invention.

[Figure 7] Portion enlarged cross section diagram of elastic roll vicinity of Figure 6.

[Figure 8] Partially cut-out oblique diagram of polymer electrolyte secondary battery which is produced by method which is shown in Figure 6.

[Figure 9] Oblique view in order to explain other production form in another polymer electrolyte secondary battery which relates to this invention.

[Explanation of Reference Signs in Drawings]

- 1... 1st lengthwise film,
- 2... 2nd lengthwise film,
- 3 and 3a, 3b ... guide plate,
- 5a, 5b ... elastic roll,
- 6... hot seal section,
- It has 7a and 7b... hot melt adhesion resin surface film
- 8 and 11... externally mounted member,
- 9, 12... polymer electrolyte secondary battery,
- 10, 10a and 10b... spacer,
- 21... unit battery,
- 22... positive electrode,

23...負極、

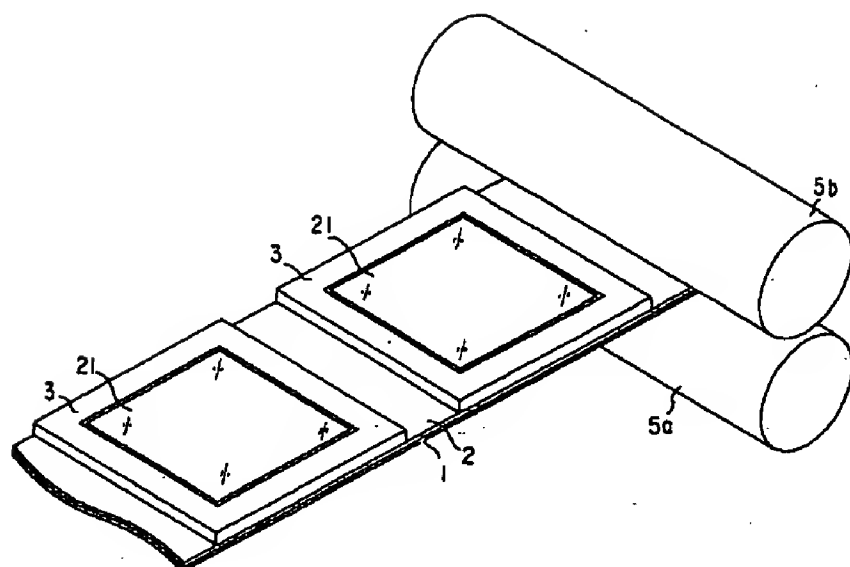
24...固体ポリマー電解質層。

23... negative electrode ,

24... solid polymer electrolyte layer .

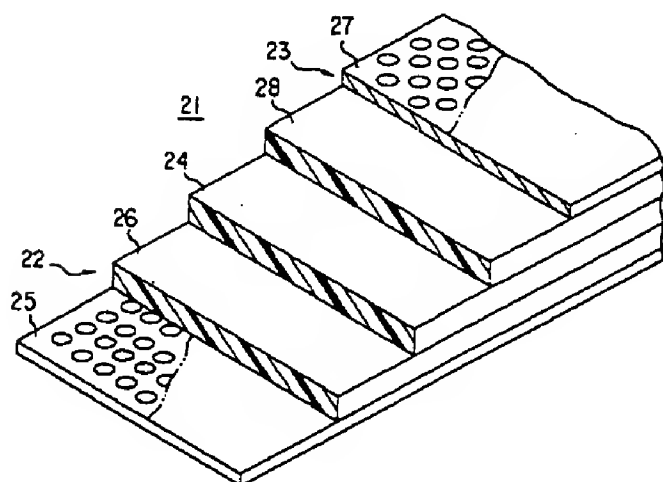
【図1】

[Figure 1]



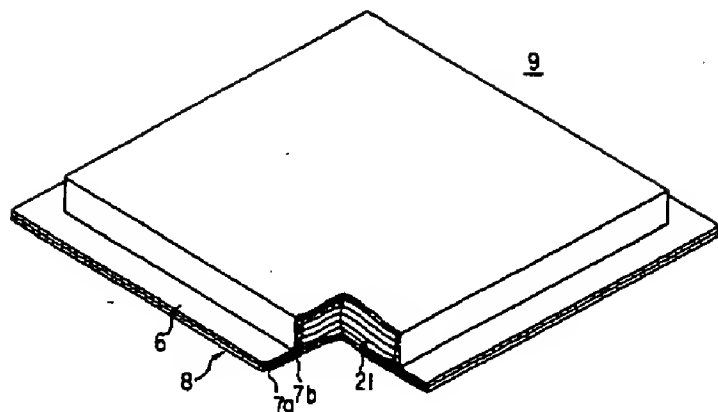
【図2】

[Figure 2]



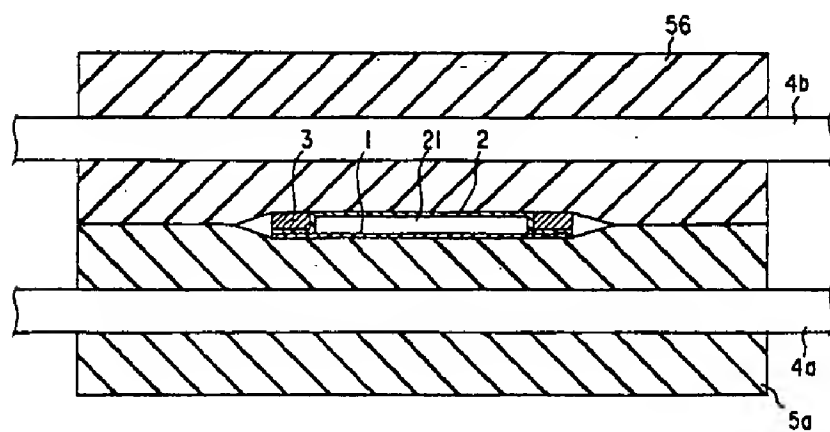
【图 4】

[Figure 4]



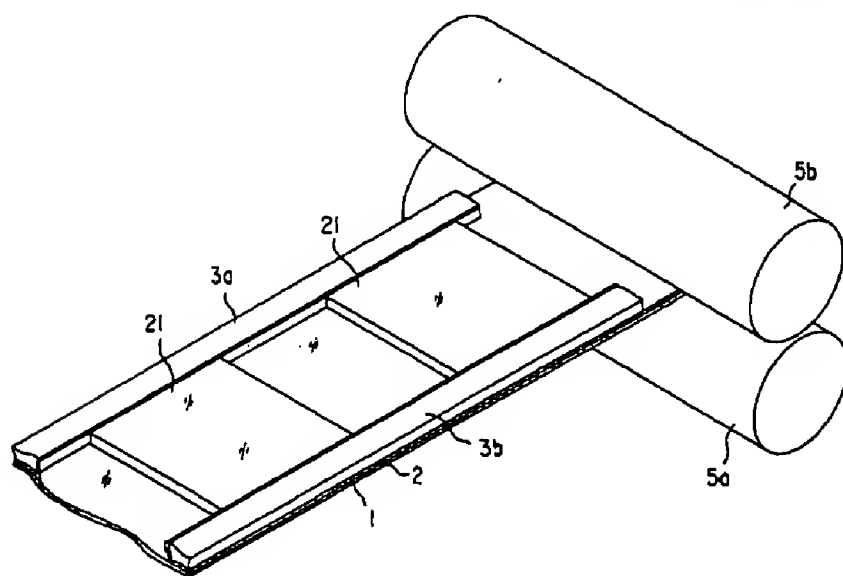
【图 3】

[Figure 3]



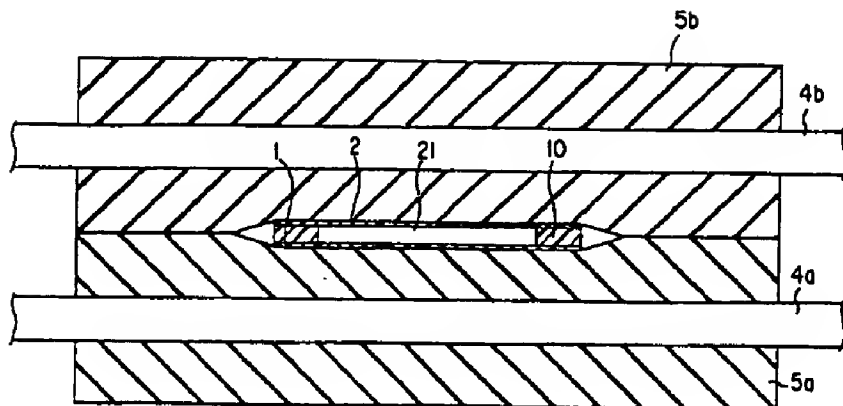
【图 5】

[Figure 5]



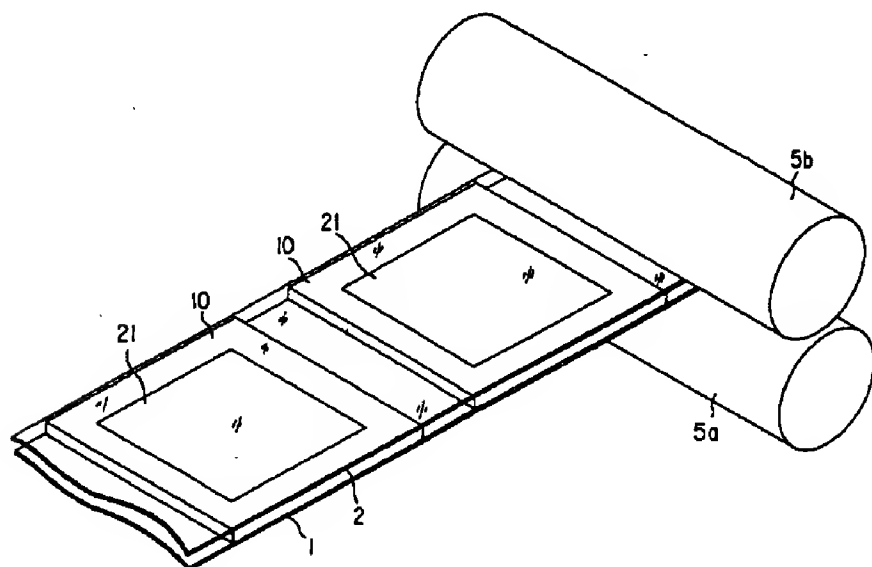
【図 7】

[Figure 7]



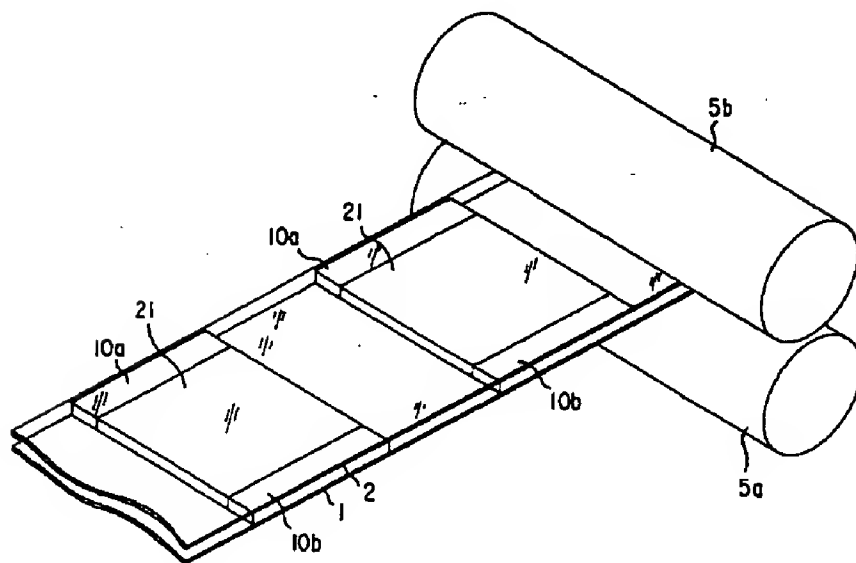
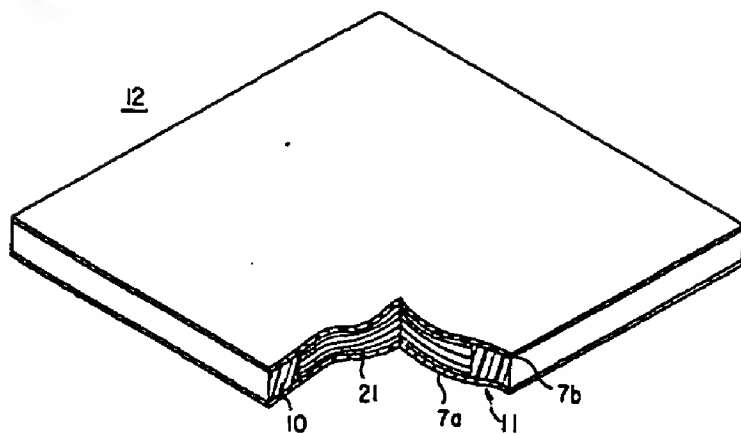
【図 6】

[Figure 6]



【図8】

[Figure 8]



【図9】

[Figure 9]